Exploring the applicability of solar driven photocatalytic processes to control infestation by zebra mussel

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Abstract

Dreissena polymorpha (zebra mussel) is an invasive freshwater bivalve mollusc that causes important technical and environmental problems. Titanium dioxide solar photocatalysis was checked for disinfestation of veligers of zebra mussel. Approximately 70% damaged larvae were observed after 2 hours of solar irradiation with 0.2 and 0.5 g/l of TiO_2. Neutral photo-Fenton could be a promising alternative as ca. 80% damaged larvae were detected in only 3 hours irradiation in the presence of H_2O_2 (10 mg/l). This process was clearly more effective than sunlight irradiation, H_2O_2, or dark Fenton. The performance of the process was slightly improved when a pH value of 5.5 was employed, although further research is needed to explore the compatibility of this medium with irrigation. Finally, the process was scaled up to 4 liters using a solar photo-reactor; again in this case, 90% of the veligers were damaged after 3 hours of irradiation.

Keywords

Photo-Fenton, sunlight, zebra mussel, titanium dioxide, infestation

1. Introduction

The zebra mussel (*Dreissena polymorpha*) is a freshwater bivalve mollusc native of the Ponto Caspian Region, in the South East of Europe; it has become an invasive species present in aquatic ecosystems of Europe (e.g. Great Britain, the Netherlands, Northern and Central Italy, Northern Spain) and North America (Great Lakes area), probably due to river navigation and unauthorized translocation of fishes between aquatic systems [1]. Their growing conditions are: dissolved oxygen above 10%, optimal temperature in the range 10-25ºC, optimal pH between 7.4 and 8.5 and between 2-14 m depth [2] The introduction of *D. polymorpha* represents important ecological threats such as alteration of river and lake ecosystems, their aggressive filtering activity can remove a large fraction of phytoplankton and zooplankton impacting the food chain, accumulation of pollutants in their tissues and substitution and extinction of native mussels [3-5]. Furthermore, this mussel also produces adverse effects on infrastructure, which result in significant economic losses [6,7]. This risk has to be minimized by preventing its introduction in areas not affected and its proliferation where it is already present. Nevertheless, the fast reproduction of *D. polymorpha* once introduced, reaching high population densities, makes the progressive colonization of natural and artificial surfaces in contact with water virtually unstoppable [1, 8]. In particular, zebra mussels have been detected in the last decade in the Ebro river basin, in the North East of Spain [9]; important damage to irrigation infrastructures in this area are attributable to this prolific mollusc, among them bio-fouling of pipelines and pumping stations, which results in significant maintenance costs.

Chlorination is the most widely employed method to control the zebra mussel population; despite its efficiency, the disadvantages related to the use of chlorine or hypochlorite (e.g. formation of halogenated organics) means that it is still necessary to explore novel approaches to deal with this threat. Moreover, the use of chemicals presents some disadvantages, such as harmful impact on non target organisms and great expense. Consequently, the main objective in research of zebra mussel control is to develop more cost-efficient and environmentally friendly solutions. Innovative application strategies and delivery methods for existing biocides (encapsulation, combination of toxins), chemical product engineering, biological methods (microbial toxins), electrical fields, pulse acoustics, low frequency electromagnetism or UV light could, in the future, be economical and environmentally acceptable tools in the control of zebra mussel colonization [10-13].

In this context, the applicability of Advanced Oxidation Process (AOP) based on sunlight deserves to be explored as it has been demonstrated to be useful for water remediation in rural areas because: a) they employ robust equipment that requires low maintenance; b) the use of hazardous chemicals can be avoided or reduced to low concentrations; and c) they benefit from the economic and ecological advantage that they use sunlight [14, 15].

Some semiconductors are able to photogenerate highly reactive species, upon irradiation; titanium dioxide is the most widely employed as heterogeneous solar photocatalyst as it is innocuous, non soluble and it is able to employ the UVB-UVA fraction of sunlight [16]. In particular, a significant number of papers have been published on the use of solar-driven TiO_2-photocatalysis for water disinfection; this information has been summarized in recent revision papers [14, 15]. Nevertheless, as far as we know, this process has only been employed for the elimination of microbiological pathogens (bacteria, fungi, protozoa, algae) but no information is available on the control of more complex species, such as molluscs.

Another attractive approach is the use of a photo-Fenton process for this purpose. This method, which uses the ability of catalytic amounts of iron to decompose the hydrogen peroxide into highly oxidizing species, namely hydroxyl radical, is greatly accelerated upon irradiation; sunlight can be employed for this purpose [17]. In fact, hydrogen peroxide has been proven to be efficient in the control of zebra mussels, although higher concentrations than for chlorine or ozone were required to reach similar mortality [18]. However, there is very limited information on the use of photo-Fenton for disinfection, as the optimal operational conditions are too aggressive (pH values slightly below 3). Nevertheless, some recent papers have dealt with the possibility of applying (photo)-Fenton processes at higher pH employing complexing agents such as citric acid or humic acids [19-22]. In addition, the less efficient neutral photo-Fenton process might be useful to remove trace pollutants or for disinfection; in fact, some recent papers have reported on the use of photo-Fenton for disinfection of *Escherichia coli* bacteria [23] and to eliminate prions [24].

With this background, the aim of this paper is to explore the effect of solar driven photo-oxidative processes on zebra mussel veligers as a first stage to determine the real applicability of these methods to prevent bio-fouling of irrigation infrastructures. Veliger is a juvenile planktonic stage of *D. polymorpha* that occurs between the age of 15 and 28 days, depending on environmental conditions, with a size between 70 and 160 μm; they were chosen because they are protected by a rudimentary shell, and chemical management strategies targeting early larval stages of *D. polymorpha* are likely to be more cost-efficient and less prone to non-target environmental impact than strategies aimed at adults [25], as adults can avoid exposure to aqueous application of some chemicals by terminating water intake via shell valve closure for periods up to 2 weeks [26].

2. Experimental

2.1. Reagents.

Titanium dioxide employed in this work was supplied by Degussa (Degussa P25). Hydrogen peroxide (30% v/v) and ferrous sulphate were purchased from Panreac and used without further purification. Other chemicals used in this work were from Panreac.

Water samples infested with veligers of *D. polymorpha* were taken from the Mequinenza Lake, on the Ebro river (Spain). They were concentrated by filtering a volume of water through a KC conical plankton net (40 cm diameter, 100 cm length) made of Nylon of mesh size of 50 micron, purchased from KC-Denmark, in order to obtain a concentration of larvae in the range 50-500 individuals/ml. Under these conditions, water containing the larvae had a total organic carbon (TOC) of 100-110 mg/l, which upon filtration gave a dissolved organic carbon (DOC) of approximately 75 mg/l. The conductivity was ca. 1400 μS/cm and the pH was close to neutrality (6.7). Samples were never stored more than 2 days before they were treated.

2.2. Treatments.

2.2.1. Lab scale tests

Preliminary (photo)-assisted treatments to eliminate zebra mussel veligers from water samples were performed in open glass vessels, loaded with aliquots of 100 ml. In the case of heterogeneous photocatalysis with TiO_2, the amount of this solid was adjusted to be within the range 0.1-0.5 g/l. In the (photo)-Fenton process, iron concentrations of 5 and 10 mg/l of iron (II) were used, added as a sulphate salt, and the initial concentration of hydrogen peroxide in the sample was adjusted to be within the range 5-340 mg/l. All treatments occurred at natural pH (ca. 7) or slightly acidified to 5.5. Samples were submitted to real sunlight; solar irradiations were performed in sunny days of June and July in the East of Spain. UVA irradiance was in all cases in the range 35-40 W/m^2. Periodically, 1 ml of the mixture was taken to be analyzed by microscopy. In the (photo)-Fenton process, the remaining concentrations of iron and hydrogen peroxide were monitored. Experiments were repeated at least twice and the error was estimated to be less than 15%.

2.2.2. Bench scale tests

Bench scale reactions were carried out in a solar photo-reactor based on cylindrical parabolic compound collectors (CPC), which has been described in detail elsewhere [27]; the irradiated surface and volume were 0.26 m^2 and 1.83 l respectively (see Figure 1). The plant was loaded with 4 l of water infested with zebra mussels and it was continuously recirculated from the reservoir to the illuminated CPCs. A photo-Fenton process was applied at the natural circumneutral pH (6.7). The initial concentrations of iron and hydrogen peroxide were 5 mg/l, and both chemicals were monitored throughout the process; when the concentration of H_2O_2 was below 1 mg/l, extra amounts of this reagent were added.

The photo-reactor was provided with a radiometer; in order to normalize the intrinsically changing conditions of solar irradiation, t_{30W} was employed; briefly, this is the time required to reach the accumulated solar irradiation at the sampling time if the irradiance were contant, namely 30 W/m^2 [28]. This parameter can be calculated according to equation 1, where UV_{ac} is the accumulated solar radiation (J/m^2), V_i the irradiated volume (l), V_t the total volume employed in the experiment: irradiated + pipes + reservoir (l); finally I is the average UV irradiance, typically 30 W/m^2 in the South East of Spain.

$$t_{30W} = \frac{UV_{ac} \cdot V_i}{I \cdot V_t} \qquad \text{(equation 1)}$$

2.3. Analysis.

The effect of the treatment on the veliger larvae was monitored by microscope. A polarized light microscope (Motic AE31) was employed for this purpose. Damaged larvae were identified because of the cleavage of their velum (this effect can be clearly appreciated in Figure 2, see supporting material for more images); based on these results, mortality was estimated. Microscopic analyses were performed immediately after sampling.

Dissolved organic carbon (DOC) in the treated solutions was determined by means of a Shimadzu model TOC-V CSH analyzer, provided with an autosampler. The concentration of iron was determined according to the o-phenantroline standardized procedure [29]. Briefly, all the iron was reduced to iron (II) by addition of hydroquinone and the pH was adjusted to 3.5; then o-phenantroline was added and the red complex formed was determined spectrophotometrically at 508 nm. Hydrogen peroxide was measured by a colorimetric method with test stripes (Merckoquant), purchased to Merck.

3. Results and discussion

3.1. TiO_2 photocatalysis.

Three different concentrations of titanium dioxide were tested (0.1 g/l, 0.2 g/l and 0.5 g/l) to disinfect samples containing zebra mussel veligers. The percentage of damaged veligers was determined by microscopic analysis after 1 and 2 hours of solar irradiation. Figure 3 indicates that damage in the velum was observed in ca. 40% of the larvae in the process driven with 0.1 g/l of photocatalyst, while this percentage was increased to more than 60% in the presence 0.2 g/l and 0.5 g/l. On the other hand, although some damaged individuals were detected in the control sample submitted to solar irradiation in the absence of TiO_2, results were poorer than those achieved in the presence of this material, showing the photocatalytic effect of TiO_2.

A comparison of the results obtained with the different TiO_2 dosages indicate that there was a certain improvement when the photocatalyst amount was increased from 0.1 g/l to 0.2 g/l. In contrast, there was no significant variation between 0.2 g/l and 0.5 g/l. This is a behaviour described for photochemical oxidation of pollutants in the presence of TiO_2 and it could be attributed to a screening effect in which the inner particles are hidden by the outer ones; these trends have also been observed in TiO_2-based disinfection, as recently reviewed [15].

Although TiO_2-photocatalysis could be useful to control zebra mussel populations and this issue deserves further research, its real applicability to prevent biofouling of irrigation pipes is limited by the impossibility of using this heterogeneous photocatalyst in slurry. Only strategies involving immobilization of particles of this material onto a suitable support could be of real interest; nevertheless, the effects on the system hydrodynamics should be carefully evaluated.

3.2. Photo-Fenton process.

3.2.1. Lab scale photo-Fenton tests

In order to overcome the inconvenience of TiO_2-based heterogeneous photocatalysis reported above, the applicablity of a solar driven process in samples of Ebro River without pH modification to control veligers of zebra mussel was investigated. For this purpose, 5 mg/l of iron(II) were added to a sample of the Mequinenza Lake infested with zebra mussels, with a concentration of hydrogen peroxide of 5 mg/l. Figure 4 shows that there was a very important effect on the larvae, as only ca. 20% of them remained undamaged after 3 hours of irradiation and this value decreased to 10% after 6 hours. Interestingly, the photo-Fenton process was able to enhance the disinfecting effect of hydrogen peroxide, as nearly 50% of the larvae kept their velum undamaged after 6 hours of treatment with H_2O_2. Dark Fenton also seemed to improve the performance of H_2O_2 although in this case the effect was not as remarkable as in the case of photo-Fenton. Although comparable results have been achieved with TiO_2 and neutral photo-Fenton under the studied experimental conditions (ca. 70% of damaged larvae) the use of homogeneous photo-Fenton appears more attractive than heterogeneous TiO_2 from the technical point of view, as stated above.

Regarding the mechanism for disinfection by (photo)-Fenton process, it has been reported in a recent review that hydrogen peroxide and iron inside the cells can catalyze the production of reactive oxygen radicals, producing important damages to cells [15]; furthermore, DNA disruption, oxidation of proteins and aminoacids and lipid peroxidation of membrane fatty acids have been proposed as toxicity mechanisms for the Fenton process [30].

The results reported above strongly suggest that a photo-Fenton process played a major role in the disinfection process, despite the low solubility of iron in the reaction medium (pH = 6.7). However, the concentration of iron was monitored throughout the experiment and it was found to remain nearly constant in the range 1-2 mg/l, while most of the rest was kept in suspension (ca. 5 mg/l were measured according to o-phenantroline method when samples were not filtered); these values were above those reported for the solubility limits of inorganic Fe(III) at pH = 7 given in literature [31]. Nevertheless, the solubility of iron depends on the composition of natural waters, as it has been reported that some chelating agents can be found among dissolved organics (e.g. humic acids), which are able to increase the solubility of this cation [32, 33]. The presence of these species is compatible with significant amounts of dissolved organics in the studied samples from the river Ebro (DOC was ca. 75 mg/l).

Regarding the effect of the concentration of hydrogen peroxide in the photo-Fenton process, experiments were run with a higher concentration of this reagent (340 mg/l). Under these conditions, the efficiency of the disinfestation process was not significantly improved as the mortality of veligers was in the range 60-70% after 2 hours of treatment. This could be attributed to a possible detrimental role of high concentrations of H_2O_2, as has been reported in the case of microorganisms, where increasing hydrogen peroxide concentrations resulted in a lower inactivation efficiency [30]. The concentration of iron was also increased to 20 mg/l. Also in this case no improvement was observed in the process, most probably due to the precipitation of the extra amounts of iron that were added (data not shown).

Another parameter that could be controlled in the process is pH. As reported above, it is well known that its optimal value for a photo-Fenton process is 2.8; nevertheless, highly acidic media are not compatible with a use of the treated solution for irrigation. However, slightly acidic pH values might be acceptable for the process, as they could be compatible with agricultural use of the treated water and the effect of the photo-Fenton would be probably enhanced. Figure 5 shows that when the pH was modified to 5.5, the performance of the process was significantly improved, as 80% of the veligers were damaged after 1 hour of treatment and no undamaged veliger was detected after 3 hours. The Fenton process was also able to disinfest the sample showing that this method could also work even in the absence of light at this pH value; H_2O_2 also had a remarkable effect on the veligers, although 20% remained undamaged after 6 hours.

The effect of the photo-Fenton on veligers under these conditions could be partly attributed to the slightly acidic media (ca. 30% of larvae were damaged after 3 hours and approximately 70% after 6 hours) as this pH value is far below the optimal range for zebra mussels (7.4-8.5) [2]. In fact, the difference between damaged individuals in the photo-Fenton process and in the control (sunlight irradiation) is 70% at neutral pH and 65% for the acidic media; hence, enhanced efficiency of photo-Fenton at pH = 5.5 should be, at least partly, atributed to the effect of pH on veligers.

3.2.1. Bench scale photo-Fenton tests

In order to gain further insight into the real applicability of solar-driven neutral photo-Fenton, a solar photo-reactor able to treat up to 4 liters of water was used. An experiment was carried out at the natural pH (6.7). Figure 6 shows that less than 20% of larvae kept their velum undamaged after ca. 120 min of normalized irradiation intensity, showing that the process might be scaled up and deserves further research. Regarding the H_2O_2 concentration, some consumption was detected and additional amounts were added at t_{30W} ca. 100 min to increase the concentration to 2 mg/l, as this concentration was observed to be below 0.5 mg/l at this irradiation time. Finally, the iron amount was found to remain approximately constant in the range of 4-5 mg/l; again in this case, its enhanced solubility should be attributed to the presence of chelating agents in the aqueous sample.

4. Conclusions

Preliminary laboratory scale experiments have demonstrated solar photocatalysis to be a promising alternative to eradicate zebra mussels from irrigation facilities, as more than 70% damaged larvae were observed after only 2 hours of treatment. Although comparable results have been achieved using TiO_2 and a circumneutral photo-Fenton process, the technical applicability of the homogeneous photo-Fenton appears easier than slurry TiO_2; in addition, the process is enhanced at slightly acidic pH, 5.5, which might be compatible with the use of disinfected water for irrigation. Bench scale experiments performed in a solar photo-reactor also showed the potential applicability of this methodology. However, further research is needed on this issue before real scale facilities can be designed, mainly on the application of phytotoxicity tests to the photo-treated effluents in order to rule out their potential toxic effect on crops to be irrigated, but also to elucidate the mechanism of attack of the reactive oxygen reactive species to the velum and to determine the real mortality that has been reached.

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Figure 1. Pilot plant for wastewater detoxification based on CPC collectors.

Figure 2a. Microscopic image of a veliger larva of *Dreissena polymorpha*. On the image below, the damaged velum of a larva killed by an oxidative treatment can be observed.

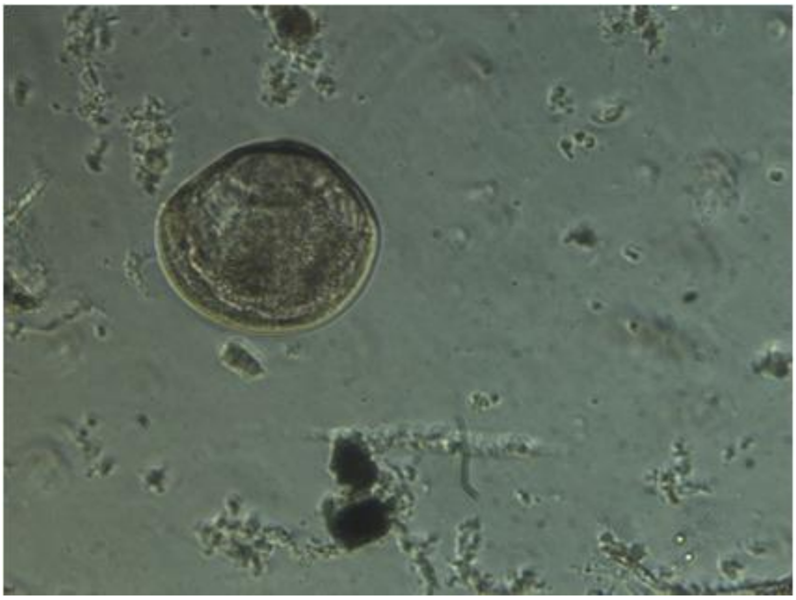


Figure 2b Damaged velum of a larva exposed to a photo-Fenton treatment.

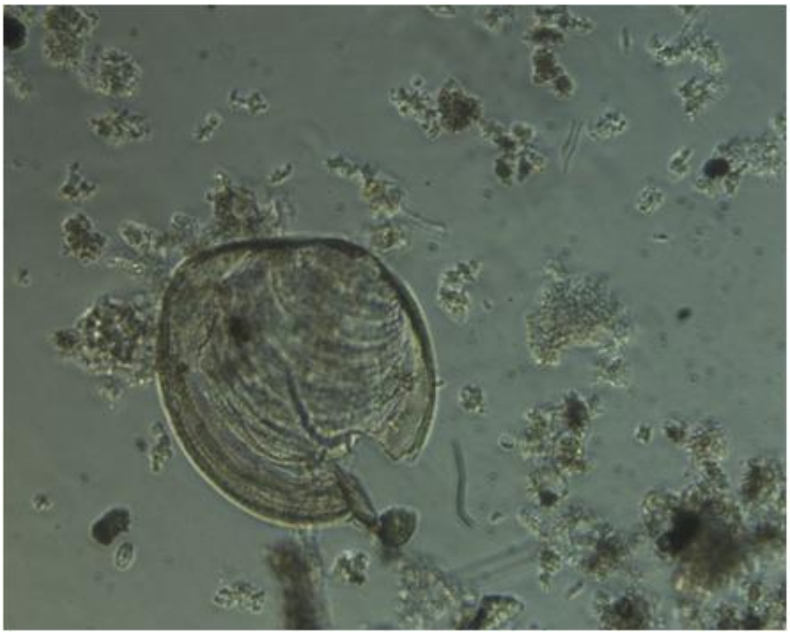


Figure 3. Undamaged veliger larvae of zebra mussel (relative values) after 60 min and 120 min of photocatalysis in the absence (×) and presence of TiO_2: 0.1 g/l (♦), 0.2 g/l (■), 0.5 g/l (▲). The initial concentration of veligers was between 100 and 300 larvae/ ml.

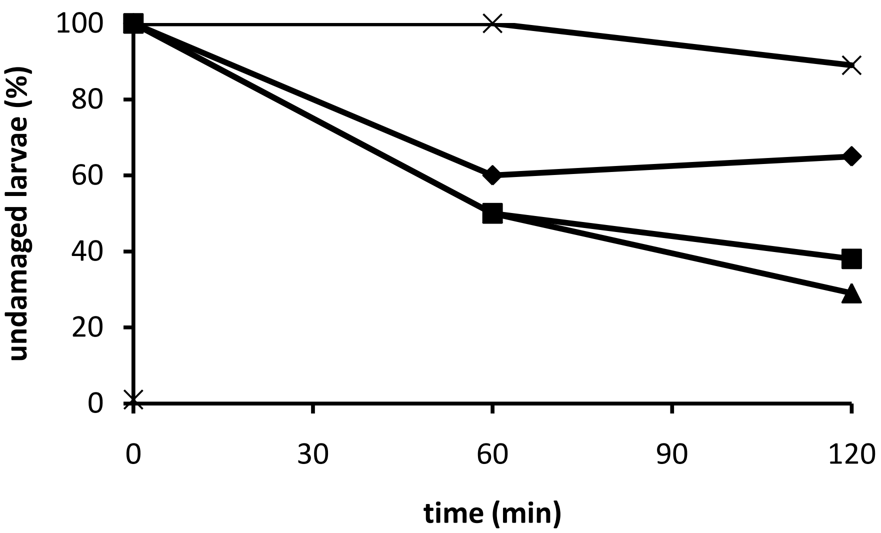


Figure 4. Plot of the percentage of undamaged veligers of zebra mussel after different times of treatment at neutral pH: photo-Fenton (5 mg/l of iron and 10 mg/l of H_2O_2, sunlight) (▲), Fenton (5 mg/l of iron and 10 mg/l of H_2O_2) (●), 10 mg/l of H_2O_2 (♦) and irradiation in the absence of the Fenton reagent (×).The initial concentration of veligers was between 80 and 120 larvae/ ml.

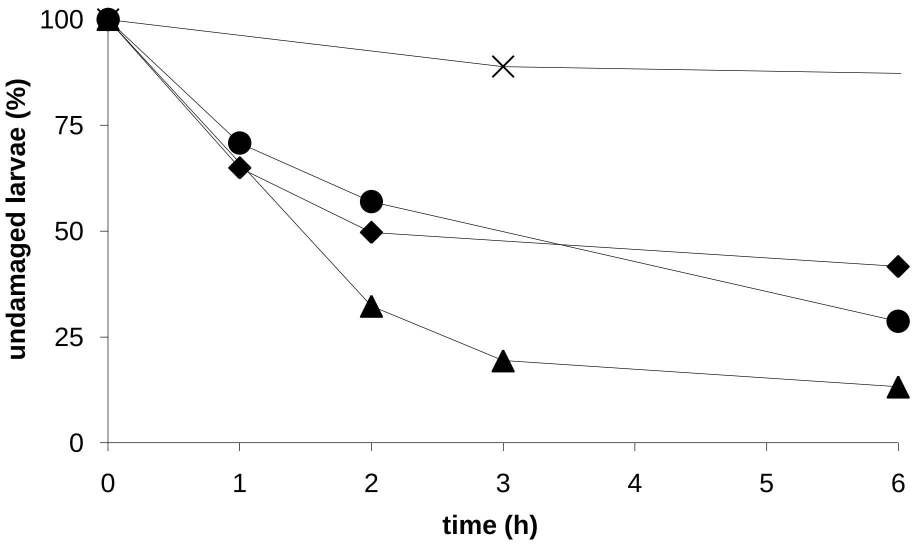


Figure 5. Plot of the percentage of live veligers of zebra mussel after different times of treatment at pH = 5.5: photo-Fenton (5 mg/l of iron and 10 mg/l of H_2O_2, sunlight) (▲), Fenton (5 mg/l of iron and 10 mg/l of H_2O_2) (●), 10 mg/l of H_2O_2 (♦) and irradiation in the absence of the Fenton reagent (×).The initial concentration of veligers was between 150 and 250 larvae/ ml.

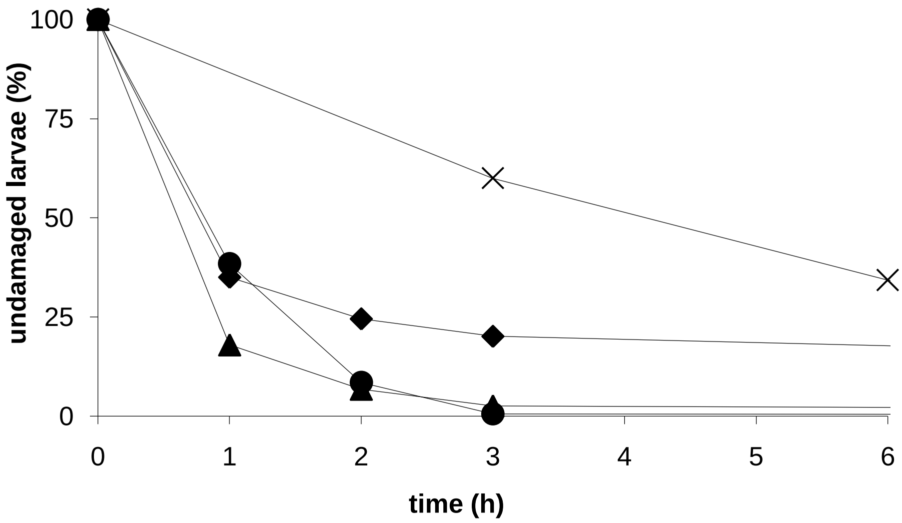
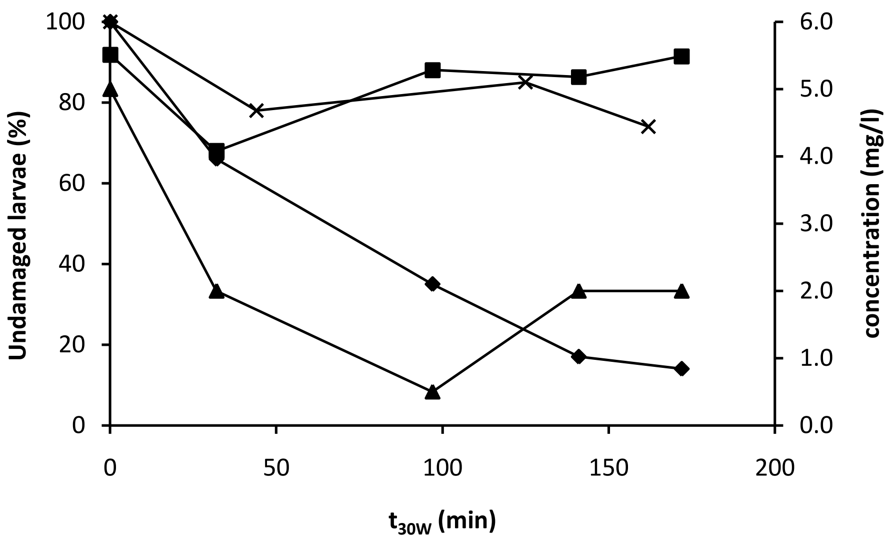


Figure 6: Pilot plant disinfection of water containg zebra mussel veligers by means of a circumneutral photo-Fenton process. Percentage of undamaged larvae (♦), and concentrations of hydrogen peroxide (▲) and iron (■) (both of them on right axis) are ploted vs. time. Undamaged larvae in the control experiment (solar irradiation) is also given (×). The initial concentration of veligers was between 50 and 100 larvae/ ml, (20 larvae/ml in the control experiment).



Supplementary Material

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