



Reclamation of agro-wastewater polluted with pesticide residues using sunlight activated persulfate for agricultural reuse

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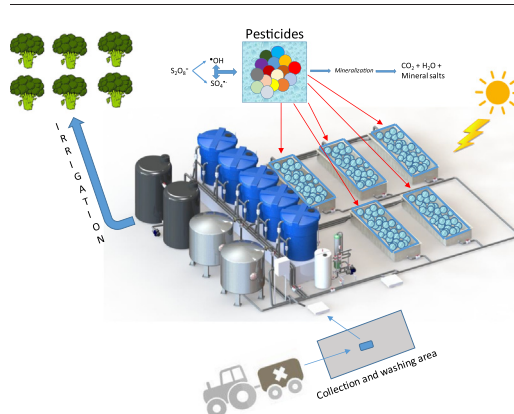
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HIGHLIGHTS

- Removal of 17 pesticides in real agro-wastewater was studied under natural sunlight.
- Persulfate photolysis was proven to be highly efficient in pesticide disappearance.
- After solar treatment the remaining percentage of pesticides was <3% of the total initial mass.
- H_{90} ranged from 30 kJ m^{-2} (spinosyns) to $76,753 \text{ kJ m}^{-2}$ for the most refractory compound (flonicamid).
- No differences in quality of broccoli were found from the use of reclaimed and usual irrigation water.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of 17 pesticides (pymetrozine, flonicamid, imidacloprid, acetamiprid, cymoxanil, thiacloprid, spinosad, chlorantraniliprole, triadimenol, tebuconazole, fluopyram, difenoconazole, cyflufenamid, hexythiazox, spiromesifen, folpet and acrinathrin) found in agro-wastewater from washing of containers and phytosanitary treatments equipment, has been carried out using sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) at pilot plant scale under natural sunlight. Persulfate is a strong oxidant, inexpensive and environmentally appropriate. However, this oxidant is slow in kinetics under ordinary conditions. $\text{Na}_2\text{S}_2\text{O}_8$ can be activated by ultraviolet light, generating $\text{SO}_4^{\bullet-}$ radicals, which are also a very strong oxidizing species ($E_0 = 2.6 \text{ V}$). Previously, preliminary experiments were carried out at laboratory scale using a photoreactor to optimize the $\text{Na}_2\text{S}_2\text{O}_8$ (300 mg L^{-1}) concentration on the rate constants of the found pesticides. The residual levels of the studied pesticides in agro-wastewater (900 L) were in the range $0.02\text{--}1.17 \text{ mg L}^{-1}$ for acrinathrin and fluopyram, respectively. After treatment, nearly complete degradation (>97%) of the parent molecules was achieved although 13% of initial DOC was measured. No significant differences ($p < 0.05$) were found when comparing grown broccoli using reclaimed and unreclaimed water.

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1. Introduction

Sustainability is the main axis of the European agrarian model, where agricultural production plays an important socio-economic role in this field. Agricultural production is supported, among other means

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of production, on phytosanitary products, which have a great economic and environmental importance. Therefore, to protect agricultural production, the use of pesticides also called plant protection products (PPP) is widespread. Pesticides have important benefits in crop protection because they combat a variety of pests, diseases and weeds that could destroy crops thus improving yields and protecting the availability, quality, reliability and price of products to the benefit of farmers and consumers.

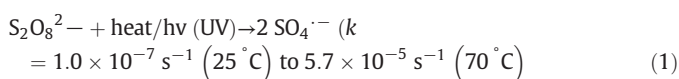
Among the 20 European Union (EU) Member States for which complete data are available, Spain, France, Italy and Germany collectively sold over 50% of the total EU pesticide sales volume reported in 2016. In terms of the categories of pesticides sold, the highest sales volumes in 2016 were for fungicides and bactericides (46%), followed by herbicides (29%), insecticides and acaricides (11%) and other PPPs (14%). In addition, these countries are the main agricultural producers in the EU, collectively accounting for about one half (46%) of the EU's total utilised agriculture area and one-half (47%) of its total arable land (FAOSTAT, 2018).

At European Union level, the principle aim is to reduce the risks and impact of pesticide use on human health and on the environment. The environmental risk of pesticide use varies considerably from one pesticide to another, depending on the intrinsic characteristics of their active substances (toxicity, persistence, etc.) and use patterns (applied volumes, application period and method, crop and soil type, etc.). Measuring the real use of pesticides would allow a better estimate of the risks by crop and region for different compartments of the environment or for human health. In this context, due to the heavy use of phytosanitary products in some countries of the EU, especially in some Mediterranean areas, a great volume of agro-wastewater containing pesticide residues from remnants of phytosanitary treatments and rinse of the machinery used is usually generated. Therefore, rinse water from machinery used to apply pesticides and remnants from leftover mixtures must be eliminated in a controlled manner without putting the health of human beings and the environment at risk according to Directive 2009/128/EC (EC, 2009) establishing the EU framework for sustainable use of pesticides. Remnants of diluted pesticides have traditionally been eliminated by spraying newly the treated area. Other alternatives are Heliosec™ and Phytobac™ systems. Heliosec is a tool designed and registered in France by Syngenta for the management and/or disposal of wastewater resulting from agrochemical treatments. Thanks to solar radiation and wind effect, the liquid contained in the bottom of Heliosec equipment evaporates leaving a thin solid layer of non-evaporable matter. This solid layer must be disposed according to the present legislation. On the other hand, in the Phytobac system, developed by Bayer CropScience experts, pesticides in the rinse water that is left over after cleaning the farmyard are degraded down by microbial degradation. However, unfortunately, both have important limitations. In the former case, an authorized agent must finally treat the residue, while in the latter the process can be very slow in some cases for biorecalcitrant pesticides (i.e. non-biodegradable). For this reason, in order to avoid phytotoxicity issues in plants, prevent contamination of surface waters and filtration of PPPs into subsurface soil, leftover treatment mixtures and rinse water from washing treatment equipment should be eliminated or degraded using specially-designed facilities or devices.

Advanced oxidation processes (AOPs) constitute a collection of well-known methods for removal of a variety of organic pollutants and pathogens in wastewater (Malato et al., 2009; Oller et al., 2011; Tsydenova et al., 2015). They are processes based on the generation of highly reactive radicals, especially the hydroxyl radical ($\bullet\text{OH}$ -AOPs), which is among the strongest oxidizing species (standard redox potential of +2.8 V vs. NHE, normal hydrogen electrode) used in wastewater treatment and offers the potential to greatly accelerate the rates of detoxification. Among AOPs, sulfate radical-based advanced oxidation

processes ($\text{SO}_4^{\bullet-}$ -AOPs) has been gaining interest as effective solution to remove organic compounds in water. $\text{SO}_4^{\bullet-}$ can be generated mainly through two precursor salts, peroxymonosulfate (PMS, HSO_5^-) and persulfate (PS, $\text{S}_2\text{O}_8^{2-}$).

The electron/hole (e^-/h^+) recombination is one of the main drawbacks in the application of heterogeneous photocatalysis using semiconductor materials as TiO_2 and others as it causes waste of energy. In the absence of a suitable electron acceptor, recombination step is predominant, and thus, it limits the quantum yield (Quiroz et al., 2011). The ability of PS is not only attributed to the promotion of charge separation ($\text{S}_2\text{O}_8^{2-} + e^- \rightarrow \text{SO}_4^{\bullet-} + \text{SO}_4^{2-}$). PS can be activated by heat, transition metals and ultraviolet light, to form stronger oxidizing free radical anion $\text{SO}_4^{\bullet-}$ ($E_0 = 2.6$ V vs. NHE) comparable to $\bullet\text{OH}$ (Eq. (1)). However, $\text{SO}_4^{\bullet-}$ has a longer lifetime ($t_{1/2} = 30\text{--}40$ μs) than the $\bullet\text{OH}$ ($t_{1/2} \leq 1$ μs), allowing more contact and transfer mass between radical and organic compounds (Olmez-Hanci and Arslan-Alaton, 2013). PS forms two $\text{SO}_4^{\bullet-}$ through scission of the O—O bond (long bond distance = 1.497 Å and low bond energy = 33.5 kcal mol⁻¹) (Wallace et al., 2002) resulting from absorption of heat energy and/or ultraviolet light (Eq. (1)), and $\bullet\text{OH}$ according to the following reactions (Matzek and Carter, 2016):



$\text{SO}_4^{\bullet-}$ react with water at all pHs forming $\bullet\text{OH}$ (Eq. (2)) which they are the primary reactive species under basic conditions (Eq. (3)). At acidic and basic pHs, $\text{SO}_4^{\bullet-}$ and $\bullet\text{OH}$ radicals are the dominant species, respectively while both radicals participate equally in reactions at neutral pHs (Matzek and Carter, 2016). Some authors have reported the effectiveness of $\text{SO}_4^{\bullet-}$ -AOPs treatments in the degradation of different organic compounds both at lab-scale (Oh et al., 2016; Yang et al., 2017; Mercado et al., 2018) and full-scale, in a real wastewater treatment plants (WWTP) tertiary step (Rodríguez-Chueca et al., 2018). In addition, the high stability and aqueous solubility and nontoxic properties of PS are beneficial to typical water treatment processes (Mora et al., 2009). Sulfate anion is generated as a principal by-product from the catalytic oxidation reaction between $\text{SO}_4^{\bullet-}$ and organic pollutants. In cases where SO_4^{2-} in water needs to be removed, ion exchange method is the most applicable technique because it is simple and effective (Haghshenoa et al., 2009).

Although the most appropriate wavelength for PS UV-activation is 254 nm due to decreased reaction time requirements compared to other wavelengths, abatement of some organic pollutants has been observed using UV-A but at lower rates (Lin and Wu, 2014; Kushnirou et al., 2019). Activation by artificial UV light might not be a promising method in industrial applications because of the high cost and the requirement of complex equipment. However, in the case of solar applications, the process is inexpensive because the use of solar radiation.

Therefore, the aim of this paper was to assess a technique to degrade 17 pesticides widely used on different vegetables and fruit crops in the Region of Murcia (SE of Spain) in agro-wastewater from washing of containers and phytosanitary treatments equipment. For this, we have developed a pilot facility for agro-wastewater decontamination using natural sunlight and sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$). Finally, treated water was used for broccoli irrigation because Spain is the largest producer of broccoli of Europe, >500,000 t per year, of which 90% is exported, with the main production area located in the Region of Murcia. In addition, consumption of broccoli is increasing steadily worldwide because of the interest in its bioactive composition and nutritive value for health promotion.

2. Materials and methods

2.1. Chemicals

Analytical standards of pesticides (>95% purity) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). FitoDolores S.L. (Murcia, Spain) supplied the commercial formulations of the pesticides. Table 1 shows the commercial products used and the main physical-chemical properties of all pesticides (AERU, 2018). Acetonitrile, methanol, formic acid, sodium persulfate, sodium chloride, anhydrous magnesium sulfate, anhydrous sodium acetate, EDTA, all with purity >98% and primary secondary amine (PSA, 40 µm particle size) sorbent were obtained from Scharlab (Barcelona, Spain). Gallic acid and vitamin C (ascorbic and dehydroascorbic) were purchased from Fluka (Steinheim, Germany) and dithiothreitol was provided by Sigma (Steinheim, Germany).

2.2. Phytosanitary treatments

Twenty-one phytosanitary treatments were carried out in the experimental farm using commercial formulations of the studied pesticides from April to June 2017. Water from the Tagus-Segura Water Transfer (DOC: 1.62 mg L⁻¹; EC: 0.87 dS m⁻¹; pH: 8.1; Total anions: 357.7 mg L⁻¹; Total cations 144.7 mg L⁻¹) was used to prepare application mixture and washing of machinery. Different volumes of wastewater (remnants and washing volumes) were accumulated after each treatment as specified in Table S1 (Supplementary Material). The total volume to treat was about 900 L. For decontamination experiment, 180 L were introduced in each of the five reaction tanks of the pilot facility.

2.3. Experimental setup at pilot plant scale

The experiment was carried out in a pilot plant previously described (Kushnirou et al., 2019) placed in Torreblanca, (Murcia, SE of Spain, latitude 38° 01' 15" N, longitude 1° 09' 56" W, elevation 90.3 m) using natural sunlight irradiation during the summer-autumn of 2017. The pilot plant consists of five open reaction tanks (300 × 100 × 40 cm) connected to water storage tanks and recovery membrane system as depicted in Fig. S1 (Supplementary Material). Briefly, the volume can be discharged individually to every reaction tank by opening the corresponding valve thus enabling to carry out five decontamination processes simultaneously. The water is transferred to the reaction tanks

by natural pressure difference. Two PVC rods are integrated on the bottom surface of the reaction tanks to improve aeration of the solution, whose frequency and duration are configured in the control unit. The tanks are drained with the aid of pump located at the bottom of a discharge vessel to which the treated solution pours following gravitational principles. The pump, which shall be activated in the control unit, pushes the water through the output circuit when the vessel where it is placed is filled up to its practical capacity. Further down in the outlet circuit a two-tank system is embedded, acting as a filter for organic and particulate matter. Finally, the plant include two tanks (2000 L each) of storage to accumulate the treated water.

The trial was initiated on 4 September 2017 with the addition of 300 mg L⁻¹ of Na₂S₂O₈ to the corresponding reaction tanks, ending on 20 October 2017 when 20,000 kJ m⁻² were accumulated. Several samples were taken at regular intervals during the photoperiod. Finally, the tanks were covered with high-density polyethylene (HDPE) film (density: 0.95 g cm⁻³ and water absorption, 24 h < 0.05%) to prevent the entry of dust or particles into the air, rainwater or bird droppings. The samples were collected in 100 mL containers and stored in darkness (4 °C) before the analysis.

2.4. Agricultural reuse of reclaimed water

The trial was conducted in a Haplic calcisol clay-loam textured (33% clay, 30% silt, 37% sand; pH 7.3, OC 1.8%; EC 7.3 dS m⁻¹; Alkalinity 398 mg CaCO₃ kg⁻¹) through eight drainage lysimeter (4 m × 3 m), according to agroclimatic conditions (semiarid climate with saline irrigation water) in the area of Torre Pacheco (Murcia, SE of Spain). The farming used was broccoli (*Brassica oleracea* L. spp. *Italica* cv. *Parthenon*) and was applied in a planting of 21 plants per lysimeter (4 m × 3 m). The cultivar *Parthenon* used in the experiment is a large and strong plant with an excellent root system. Drip irrigation was used at 30 emitters of 3 L h⁻¹ per lysimeter. Table S2 (Supplementary Material) shows the irrigation program followed. The growing season was autumn-winter and it lasted about 100 days (October 2017 to January 2018). The cultivation was conducted following the General Standards of Integrated Pest Management in Region of Murcia (CARM, 2012).

2.5. Analytical determinations

Water samples were extracted with CH₂CN according to the procedure described by Fenoll et al. (2011). Soil samples were extracted

Table 1
Physical-chemical properties of the pesticides found in agro-wastewater.

Commercial formulation	Active ingredient ¹	Formula	MW (g mol ⁻¹)	Log K _{OW}	VP (mPa)	Water Sol (mg L ⁻¹)
Epik 20%	Acetamiprid ^A	C ₁₀ H ₁₁ ClN ₄	222.7	0.80	1.7 × 10 ⁻⁴	2950
Rufast 7.5%	Acrinathrin ^I	C ₂₆ H ₂₁ F ₆ NO ₅	340.5	6.30	4.4 × 10 ⁻⁵	0.0022
Altacor 35%	Chlorantraniliprole ^I	C ₁₈ H ₁₄ BrCl ₂ N ₅ O ₂	483.2	2.86	6.3 × 10 ⁻⁹	0.9
Elio 10%	Cyflufenamid ^F	C ₂₀ H ₁₇ F ₅ N ₂ O ₂	412.4	4.70	3.5 × 10 ⁻²	0.5
Fosbel 4%	Cymoxanil ^F	C ₇ H ₁₀ N ₄ O ₃	198.2	0.67	1.5 × 10 ⁻¹	780
Ceremonia 25%	Difenoconazole ^F	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃	406.3	4.36	3.3 × 10 ⁻⁵	15
Teppeki 50%	Fonicamid ^I	C ₉ H ₆ F ₃ N ₃ O	229.2	0.24	9.4 × 10 ⁻⁴	5200
Luna Devotion 25%	Fluopyram ^{F,N}	C ₁₆ H ₁₁ ClF ₆ N ₂ O	396.7	3.30	1.2 × 10 ⁻³	16
Fosbel 25%	Folpet ^F	C ₉ H ₄ Cl ₃ NO ₂ S	296.5	3.02	2.1 × 10 ⁻²	0.8
Exitox 10%	Hexythiazox ^A	C ₁₇ H ₂₁ ClN ₂ O ₂ S	352.9	2.67	1.3 × 10 ⁻³	0.5
Confidor 20%	Imidacloprid ^I	C ₉ H ₁₀ ClN ₅ O ₂	255.7	0.57	4.0 × 10 ⁻⁷	610
Plenun 50%	Pymetrozine ^I	C ₁₀ H ₁₁ N ₅ O	217.3	-0.19	4.2 × 10 ⁻³	270
Spintor 48%	Spinosad ^I	(A) C ₄₁ H ₆₅ NO ₁₀ (D) C ₄₂ H ₆₇ NO ₁₀	731.9 745.9	3.90 4.30	2.0 × 10 ⁻² 4.0 × 10 ⁻³	14.5 0.8
Oberon 24%	Spiromesifen ^I	C ₂₃ H ₃₀ O ₄	370.5	4.20	5.7 × 10 ⁻²	29
Orius 25%	Tebuconazole ^F	C ₁₆ H ₂₂ ClN ₃ O	307.8	3.70	1.3 × 10 ⁻³	36
Calipso 48%	Thiachloprid ^I	C ₁₀ H ₉ ClN ₄ S	252.7	1.26	3.0 × 10 ⁻⁷	184
Luna Devotion 25%	Triadimenol ^F	C ₁₄ H ₁₈ ClN ₃ O ₂	295.8	3.18	5.0 × 10 ⁻⁴	72

¹ A: Acaricide; F: Fungicide; I: Insecticide; N: Nematicide.

with CH₃CN/H₂O following the method published by Fenoll et al. (2012). Multiresidue QuEChERS procedure involving two simple steps was used to isolate pesticide residues on broccoli. First, the homogenized samples (10 g) are extracted and partitioned using CH₃CN (10 mL), 6.0 g ± 0.3 g anhydrous MgSO₄ and 1.5 g ± 0.1 g anhydrous C₂H₃O₂Na. Then, the supernatant (1 mL) is further extracted and cleaned using a dispersive solid phase extraction with 50 mg PSA and 150 mg anhydrous MgSO₄. Both extracts were analysed by HPLC-MS² and GC-MS. Blank samples were used to establish the limit of detection (LOD) and the limit of quantification (LOQ). The limit of detection (LOD) was determined as the concentration generating a peak area three-fold higher than the noise of the baseline (S/N = 3) at the retention time of the peak of interest. The LOQ was determined by multiplying the LOD by a factor of 3.3. Tables S3 and S4 (Supplementary Material) summarizes the chromatographic conditions used.

HPLC-MS². An Agilent Series 1200 liquid chromatograph (Agilent Technologies, Santa Clara, CA, USA) interfaced to a G6410A triple quadrupole mass spectrometer from Agilent equipped with an ESI interface operating in positive ion mode was used. Five microliter were injected and the pesticides were chromatographically separated using a reversed phase C8 analytical column of 150 mm × 4.6 mm and 5 mm particle size (Zorbax Eclipse XDB-C8) which was maintained at 25 °C. Mobile phases A and B were CH₃CN and 0.1% HCOOH, respectively. The optimized chromatographic method held the initial mobile phase composition (10% A) constant for 5 min, followed by a linear gradient to 100% A after 35 min. Two single reaction monitoring (SRM) transitions for quantitation and confirmation were monitored for every pesticide.

GC-MS. An Agilent HP 6890 gas chromatograph (Waldbronn, Germany) equipped with a 5973 N mass spectrometer and automatic split-splitless injector Agilent 7683 was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from *m/z* 50 to 500 at 3.21 s per scan. The ion source temperature was 230 °C, and the quadrupole temperature was 150 °C. The electron multiplier voltage (EM voltage) was maintained at 1300 V, and a solvent delay of 4.5 min was employed. An HP 5MS fused silica capillary column (30 m × 0.25 mm i.d.) and 0.25 mm film thickness, supplied by Agilent Technologies, was used. The column temperature was maintained at 70 °C for 2 min and then programmed at 25 °C min⁻¹ to 150 °C, increased to 200 °C at a rate of 3 °C min⁻¹, followed by a final ramp to 280 °C at a rate of 8 °C min⁻¹, and held for 10 min. One microliter of sample was injected in splitless mode. Analysis was performed with selected ion monitoring (SIM) mode using primary and secondary ions. Pesticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier to target ratios.

DOC. The progress of mineralization was monitored measuring dissolved organic carbon (DOC) content on a Multi N/C 3100 TOC Analyzer (Analytic Jena AG, Jena, Germany) equipped with an NDIR detector (950 °C) after sample filtration (0.45 μm).

Colour, phenolic compounds and vitamin C. For colour determinations, fresh material was triturated and analysed in triplicate using a Thermo Fisher Scientific Helios-Omega spectrophotometer (Pittsburgh, PA). Measurements were performed in the CIEL*a*b* system. Lightness value, L*, indicates how dark/light the sample is (varying from 0-black to 100-white), a* is a measure of greenness/redness (varying from -60 to +60), and b* is the grade of blueness/yellowness (also varying from -60 to +60). Phenolic compounds were extracted with methanol: formic acid (97:3) and the total phenolic content was determined by the Folin-Ciocalteu method. The phenolic concentration was calculated by recording the optical density of each sample at 765 nm in a Shimadzu UV-2401PC spectrophotometer (Kyoto, Japan), and comparing it with a standard curve of gallic acid. Vitamin C (ascorbic and dehydroascorbic) was extracted from fresh material with EDTA, 0.05% (w/v) and dithiothreitol and analysed by HPLC-MS/MS according to the methodology developed by Fenoll et al. (2011).

2.6. Kinetic parameters

Assuming a pseudo-first-order kinetics and using fluence ($H = dE/dA$, i.e. the radiant energy received by the reaction tanks per unit area) units the apparent rate constant (k_{app}) can be obtained from the Eq. (4):

$$C_H = C_0 \cdot e^{-k_{app} \cdot H} \text{ or } \ln(C_0/C_H) = k_{app} \cdot H \rightarrow \ln(1-X) = k_{app} \cdot H \quad (4)$$

where k_{app} is the apparent reaction rate constant (in m² kJ⁻¹), H is the fluence (accumulated UV-A radiation in kJ m⁻²), C_0 the initial concentration of pesticide (mg L⁻¹) and C_H is the residual concentration of pesticide at fluence H . The advantage of using fluence units is the possibility of comparing results between different studies.

Consequently, the fluence required for $X\%$ of pesticide to disappear from the water due to degradation processes alone can be calculated following Eq. (5):

$$H_x = \ln(100/(100-X))/k_{app} \quad (5)$$

2.7. Statistical analysis

Results are presented as the mean values ± standard deviation (SD). The SigmaPlot v 13.0 statistical software package (Systat Software Inc., San José, CA) was used for curve fitting and performing statistical analyses. In order to determine significant differences between the means of the treatments, data was subjected to one-way ANOVA ($p < 0.05$) using the IBM-SPSS Statistics version 23 software (Armonk, NY).

3. Results and discussion

3.1. Preliminary experiments

Preliminary experiments (unpublished data) were carried out at lab-scale using the photoreactor described in a previous paper (Vela et al., 2015) to assess the influence of the Na₂S₂O₈ concentrations on the rate constant of the studied pesticides. As result, the degradation rate significantly increases by adding the Na₂S₂O₈ (0–300 mg L⁻¹). However, no significant differences ($p < 0.05$) were observed when the oxidant loading was increased from 300 to 500 mg L⁻¹. Thus, 300 mg L⁻¹ of Na₂S₂O₈ were used in the further experiments at pilot plant scale.

3.2. Photodegradation of pesticides at pilot plant scale

Fig. 1 shows the evolution of pesticide concentrations (C_H/C_0) as a function of fluence. As can be observed, after 2235 kJ m⁻² of accumulated UV-A radiation only flonicamid (0.74), folpet (0.26), fluopyram (0.14), chlorantraniliprole (0.08) and acetamiprid (0.03) have values higher than 0.01. When 7500 kJ m⁻² were accumulated, the degradation of all pesticides was higher than 90% with the exception of flonicamid. According to the initial concentration recovered for each pesticide determined by chromatographic techniques ranged from 0.02 (acrinathrin) to 1.17 mg L⁻¹ (fluopyram), the total initial mass of pesticides was 8.5 mg L⁻¹. At the end of the experiment when 20,000 kJ m⁻² were recovered only four pesticides were detected above their respective LODs ranging from 0.002 mg L⁻¹ (fluopyram) to 0.21 mg L⁻¹ (flonicamid) as showed in Table 2. Therefore, after 42 days, the remaining percentage of pesticides was <3% of the total initial mass. After solar treatment, the initial content of DOC (23 mg L⁻¹) in agro-wastewater was reduced by 87%. The percentage remaining (about 3 mg L⁻¹) can be mainly due to the presence of flonicamid residues, adjuvants in commercial products and some recalcitrant intermediates generated during the decomposition of the parent compounds. As pesticides disappear, the electrical conductivity was weakly increased (about 0.4 units) due to the evolution of some inorganic ions

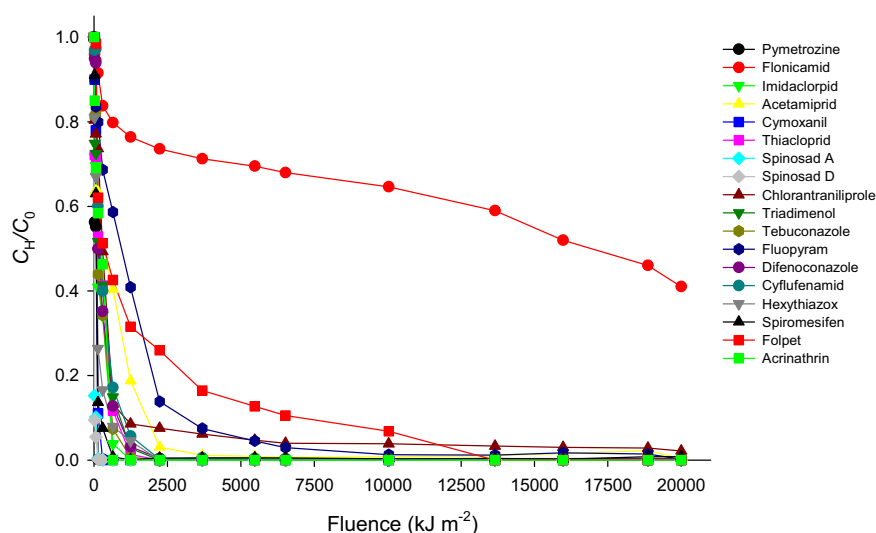


Fig. 1. Evolution of pesticide concentrations (C_t/C_0) as a function of fluence (H).

as SO_4^{2-} . In our case, the initial content of SO_4^{2-} (192 mg L^{-1}) was increased to 332 mg L^{-1} at the end of the treatment due to decomposition of $\text{S}_2\text{O}_8^{2-}$.

Flonicamid has high water solubility ($>5 \text{ g L}^{-1}$), is stable to aqueous photolysis, and is very persistent to aqueous hydrolysis (AERU, 2018). This insecticide has been shown to be not persistent in soil but moderately persistent in water (PMRAH, 2011) although it has relatively low potential for aquatic toxicity in the environment (Shelgren, 2006). Chlorantraniliprole is considered persistent in surface water and displays relatively high aquatic toxicity (Bireley and López, 2008). It is slightly soluble in water (0.9 mg L^{-1}) but it has low vapour pressure (6.3×10^{-9}). Photocatalytic experiments showed that the addition of semiconductors in tandem with sodium persulfate as electron acceptor, greatly improved the elimination of chlorantraniliprole in water compared to photolytic tests (Fenoll et al., 2015a). According to other authors, acetamiprid showed lower persistence in degradation rate in photolysis and photocatalysis ($\text{TiO}_2/\text{Na}_2\text{S}_2\text{O}_8$) processes than other neonicotinoid insecticides such as thiamethoxam and imidacloprid due to the presence of a nitroguanidine functional group in both, whereas acetamiprid, containing a cyanoimine group, was more stable

to degradation (Banić et al., 2014; Fenoll et al., 2015b). Finally, the aqueous photodegradation of fluopyram was investigated under simulated sunlight irradiation showing that its photodegradation was faster in neutral solution than that in acidic and alkaline solutions. The photodegradation rates of fluopyram in presence of Fe^{3+} and TiO_2 were about 7-fold and 13-fold faster than that without them, respectively (Dong and Hu, 2016).

As previously indicated, PS can be activated by heat and ultraviolet light to form $\text{SO}_4^{\bullet-}$ radicals. In a previous work we have observed a significant increment (about 2.4-fold) on the degradation rate of different pesticides when temperature was increased from $25 \text{ }^\circ\text{C}$ to $35 \text{ }^\circ\text{C}$ in darkness although higher degradation rates were observed under sunlight conditions for both temperatures (Kushnirou et al., 2019). Reaction mechanisms of $\text{SO}_4^{\bullet-}$ reactions differ somewhat from those of $\bullet\text{OH}$. $\text{SO}_4^{\bullet-}$ reacts more readily by electron transfer than $\bullet\text{OH}$, but slower by H-abstraction and addition. Therefore, reactivity, product patterns, and energy efficiency of $\text{SO}_4^{\bullet-}$ -based oxidation may also be different from $\bullet\text{OH}$ -based oxidation. Thus, some authors have demonstrate that some chlorotriazine pesticides such as atrazine, propazine, and terbuthylazine are very reactive with

Table 2

Dissipation of pesticide residues in agro-wastewater as a function of fluence during the experiment.

Pesticide	Accumulated radiation (kJ m^{-2})						
	0	300	600	1000	5000	10,000	20,000
	Residue levels (mg L^{-1}). In parentheses % remaining						
Acetamiprid	1.056	0.541 (51.2)	0.426 (40.3)	0.198 (18.8)	0.009 (0.9)	0.005 (0.5)	0.003 (0.3)
Acrinathrin	0.020	0.001 (5.0)	BDL	BDL	BDL	BDL	BDL
Chlorantraniliprole	0.252	0.124 (49.2)	0.033 (13.1)	0.007 (2.8)	0.012 (4.8)	0.008 (3.2)	0.003 (1.2)
Cyflufenamid	0.059	0.024 (40.7)	0.010 (16.9)	0.003 (5.1)	BDL	BDL	BDL
Cymoxanil	0.067	BDL	BDL	BDL	BDL	BDL	BDL
Difenoconazole	0.492	0.173 (35.2)	0.063 (12.8)	0.015 (3.0)	0.001 (0.2)	BDL	BDL
Flonicamid	0.509	0.426 (83.7)	0.406 (79.8)	0.389 (76.4)	0.361 (70.9)	0.331 (65.0)	0.209 (41.1)
Fluopyram	1.171	0.804 (68.7)	0.687 (58.7)	0.478 (40.8)	0.053 (4.5)	0.015 (1.3)	0.002 (0.2)
Folpet	0.099	0.051 (51.5)	0.042 (42.4)	0.039 (39.4)	0.014 (14.1)	0.007 (7.1)	BDL
Hexythiazox	0.032	0.005 (15.6)	0.003 (9.4)	0.001 (3.1)	BDL	BDL	BDL
Imidacloprid	0.785	0.268 (34.1)	0.030 (3.8)	BDL	BDL	BDL	BDL
Pymetrozine	1.140	0.020 (1.8)	0.001 (0.1)	BDL	BDL	BDL	BDL
Spinosad A	0.692	BDL	BDL	BDL	BDL	BDL	BDL
Spinosad D	0.423	BDL	BDL	BDL	BDL	BDL	BDL
Spiromesifen	0.100	0.008 (8.0)	0.001 (1.0)	0.002 (2.0)	0.001 (1.0)	BDL	BDL
Tebuconazole	0.505	0.173 (34.3)	0.037 (7.3)	0.003 (0.6)	BDL	BDL	BDL
Thiachloprid	0.785	0.324 (41.3)	0.091 (11.6)	0.010 (1.3)	BDL	BDL	BDL
Triadimenol	0.341	0.141 (41.3)	0.051 (15.0)	0.009 (2.6)	BDL	BDL	BDL

BDL: Below Detection Limit (ranging from $0.03 \text{ } \mu\text{g L}^{-1}$ for tebuconazole to $1.51 \text{ } \mu\text{g L}^{-1}$ for acrinathrin).

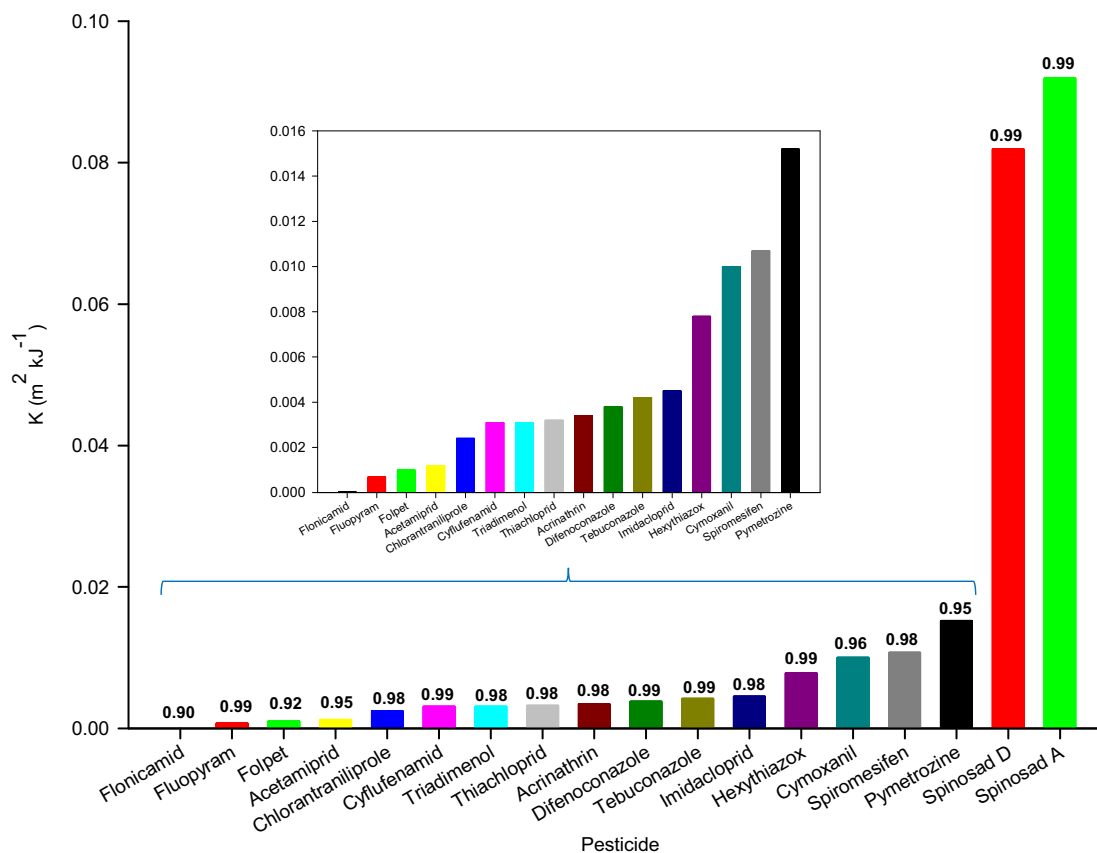


Fig. 2. Rate constants for the studied pesticides. Numbers on the bars show R^2 values for the fitting.

sulfate radicals ($2.2\text{--}3.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), while the dealkylated products of chlorotriazine pesticides are less reactive toward sulfate radicals (Lutze et al., 2015). On the other hand, Khan et al. (2017)

proposed different mechanisms for the degradation of the chlorinated pesticide lindane via $\cdot\text{OH}$ or $\text{SO}_4^{\cdot-}$ attack based on the detected by-products.

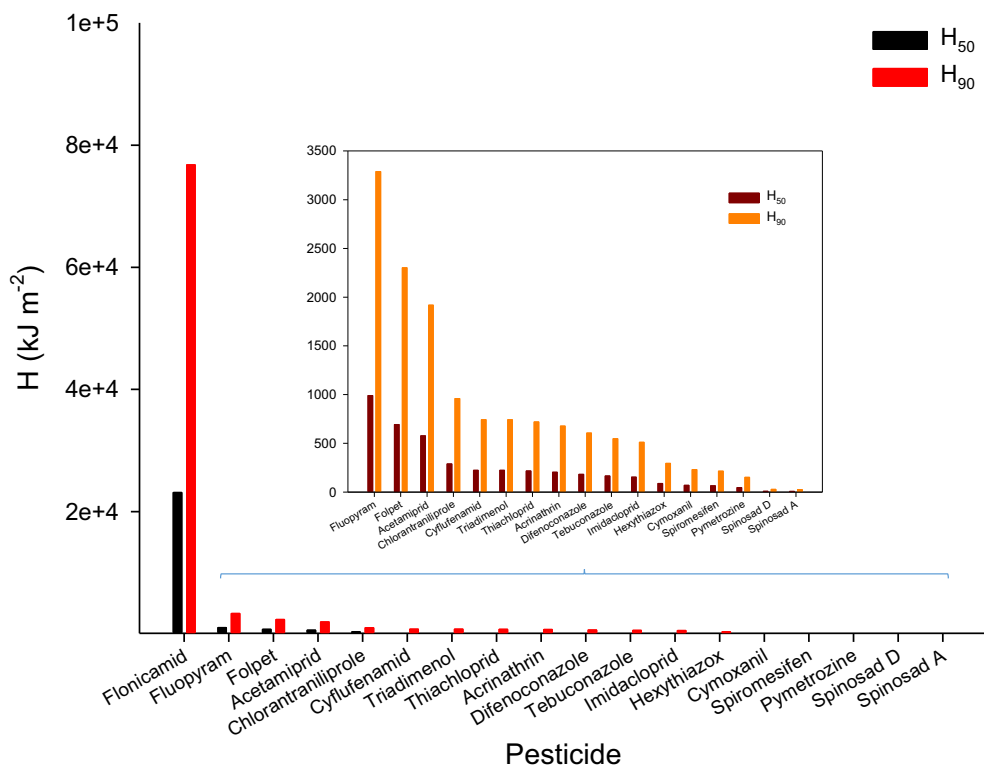


Fig. 3. The fluence to get a 50% (H_{50}) and 90% reduction (H_{90}) of the initial concentration in polluted water for each one of the studied pesticides.

Table 3

Colour parameters, phenolic compounds, vitamin C, mean diameter and weight of the vegetables after harvesting as a function of water source used for irrigation.

Water source	Parameter (Mean \pm SD)							
	Colour			Total phenolic compounds (mg g ⁻¹)	Vitamin C (mg 100 g ⁻¹)	Weight (g)	Diameter (cm)	Total yield (g)
	L*	a*	b*					
Only transfer	45.3 \pm 2.0 ^a	-9.6 \pm 1.5 ^a	14.3 \pm 3.3 ^a	0.65 \pm 0.05 ^a	67.4 \pm 2.9 ^a	362.2 \pm 120.2 ^a	17.4 \pm 2.8 ^a	30,424
Treated + transfer	44.7 \pm 2.1 ^a	-10.5 \pm 1.5 ^a	14.0 \pm 2.8 ^a	0.63 \pm 0.09 ^a	65.6 \pm 3.2 ^a	388.0 \pm 159.0 ^a	16.9 \pm 2.7 ^a	32,594

Means in the same column having the same letters are not significantly different at $p > 0.05$; SD: standard deviation ($n = 3$).

3.3. Photoreaction kinetic

The experimental values were fitted to the proposed model using the software (SigmaPlot v.13) supplied by Systat Software Inc. (San José, CA). Fig. 2 shows kinetic parameters. As can be observed, the coefficient of determination (R^2) ranged from 0.90 to 0.99 with standard error of estimate ($S_{y/x}$) lower than 7 in the most unfavourable case.

As depicted in Fig. 2 both spinosyns showed a high rate constant compared with the other studied pesticides. Spinosad is a biopesticide with insecticide properties based on a chiral molecule found in the bacterial species *Saccharopolyspora spinosa*. It is a mixture of spinosyn A (C₄₁H₆₅NO₁₀) as majority and spinosyn D (C₄₂H₆₇NO₁₀). Hexythiazox, cymoxanil, spiromesifen and pymetrozine had rate constants ranging from 0.0078 (hexythiazox) to 0.0152 (pymetrozine), while the rest of pesticides had rate constants ≤ 0.0045 .

On the other hand, the total fluence (kJ m⁻²) to get a 50% (H₅₀) and 90% reduction (H₉₀) for each one of the pesticides studied is depicted in Fig. 3. For spinosyns, the H₉₀ is lower than 30 kJ m⁻², while for the rest of pesticides ranged from 151 kJ m⁻² (pymetrozine) to 76,753 kJ m⁻² (flonicamid).

3.4. Agricultural reuse of reclaimed water for broccoli irrigation

Pesticide residues present in reclaimed water may pose risks to soil, water and biota, which will depend on the quality of the reclaimed water, the physical-chemical characteristics of the soil, the climate, the related aquifers and the irrigation practices. Table 3 shows broccoli colour parameters, mean diameter, phenolic compounds, vitamin C and weight of the vegetables measured after harvesting. Broccoli colour is the characteristic with most influence on consumer choice. As can be observed no significant differences ($p < 0.05$) were observed in any case for parameters included in Table 3. None of the studied pesticides was detected neither in broccoli nor and soil after harvesting. In addition, any pesticide was found in leaching water. As reviewed by Paranychianakis et al. (2014), some studies have shown that the uptake, translocation and accumulation of a wide range of organic pollutants in crop tissues is in overall low and does not pose significant risks for public health. In addition, plants possess metabolic pathways that might transform and degrade pollutants further decreasing the potential risks.

4. Conclusions

Agriculture generates a large volume of agro-wastewater produced in particular from the cultivation of crops to which pesticides are intensively applied. Reuse of appropriately treated wastewater for irrigation or aquifer recharge is considered to have a lower environmental impact as compared with other alternative water supplies such as water transfers or desalination. In addition, the regeneration of wastewater is a solution to increase the water resources in regions with problems of water shortage. In this context, AOPs are able to enhance the biotreatability of agro-wastewater. AOPs involve in-situ generation of highly reactive free radicals, such as hydroxyl ($\bullet\text{OH}$) or sulfate ($\text{SO}_4^{\bullet-}$). Among the various methods available for the generation of those radicals, photolysis of PS ($\text{S}_2\text{O}_8^{2-}$) has gained considerable importance in recent years, as it is an environmentally friendly and cost-effective method to oxidize

refractory pollutants like many pesticides into less harmful substances ultimately leading to the mineralization of the parent compounds to carbon dioxide and water. In addition, the use of a renewable energy source like sunlight gives the process added benefit, mainly in Mediterranean basin where many places reach >3000 h of sunlight per year. The obtained results confirm that the use of PS is an effective and low-cost method to degrade the studied pesticides in agro-wastewater in reasonable time, being able to reuse treated water for broccoli irrigation without reducing the quality of harvested product or risks to human health.

Conflicts of interest

There are no conflicts to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2019.01.060>.

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