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Research article

Reclamation of agro-wastewater polluted with thirteen pesticides by solar photocatalysis to reuse in irrigation of greenhouse lettuce grown

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ABSTRACT

In Mediterranean countries, reuse of reclaimed water is essential for crop irrigation. The occurrence of pesticides in agro-wastewater may represent a risk for human health and environment owing to their release in soil and translocation to plants. The novelty of this work relies on the reuse of reclaimed agro-wastewater polluted with thirteen pesticides for lettuce irrigation. Removing of pesticide residues in agro-wastewater was carried out using natural sunlight and $TiO_2/Na_2S_2O_8$ in a pilot facility located in Murcia (SE of Spain). The studied pesticides were azoxystrobin, boscalid, chlorpropham, flutolanil, flutriafol, isoxaben, methoxyfenozide, myclobutanil, napropamide, prochloraz, propamocarb, propyzamide and triadimenol, which are commonly used in southeast Spain to treat lettuces grown. Different heterogeneous and homogeneous processes were studied and compared. Previously, the optimization of the process for the selection of the best catalytic system was performed at lab-scale. $TiO_2 + S_2O_8^{2-}$ was selected due to the greater effectiveness, achieving almost complete disappearance after about 400 kJ m^{-2} of cumulative UVA exposure. No significant differences were observed in quality parameters of lettuce grown using treated and non-treated agro-wastewater.

1. Introduction

Currently, water shortage due to the climate change and population growth is one of the main challenge in the world of the 21st century. Agricultural sector is the largest consumer of water. In arid and semiarid regions like some Mediterranean countries, in response to water scarcity, reclaimed wastewater is being required for agriculture purposes (Lavrnic et al., 2017). However, treated wastewater for crop irrigation usually contains organic pollutants, such as pesticides, due to inefficient removal in wastewater treatment plants (Martínez-Piernas et al., 2018). These chemicals, once in the soil, could potentially be transferred to plants through root uptake and translocation, creating a potential risk when they enter into the food chain. Pesticide properties, weather conditions, soil characteristics and agricultural practices are important parameters in plant uptake of this kind of pollutants (Wu et al., 2015). The octanol-water partition coefficient (log K_{ow}) for non-ionic compounds has been recognized as a reliable predictor of uptake behaviour (Tanoue et al., 2012).

Phytosanitary products help farmers to protect their crops from pests, weeds and diseases. However, their use generate an abundant volume of wastewater containing residues of plant protection products from remnants and rinse of the treatment machinery. This wastewater should be efficiently treated by innovate technologies environmentally friendly for reuse in crop irrigation (Fenoll et al., 2019; Vela et al., 2019).

In line with this, Advanced Oxidation Technologies (AOTs), such as heterogeneous photocatalysis using TiO_2 or ZnO as photocatalysts and Fenton-type systems using Fe^{2+} or Fe^{3+} have been commonly used for pesticide degradation (Ahmed et al., 2011; Malato et al., 2009; Mirzaei et al., 2017; Rahim Pouran et al., 2015) during the last years. These technologies are based on the generation of powerful oxidizing species, mainly hydroxyl radical ($HO^{\bullet}$), one of the strongest oxidants known (E_0 = 2.8 V *vs* NHE at pH = 7). It can rapidly and efficiently destroy pesticides into CO_2, H_2O and mineral salts (Antoniou et al., 2008). Up to our

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Table 1
Physical-chemical properties of the pesticides studied.

Commercial formulation	Active ingredient	Formula	MW (g mol^{-1})	Log K_{OW}	VP (mPa)	Water Solubility (mg L^{-1})
Ortiva 25%	Azoxystrobin[F]	$C_{22}H_{17}N_3O_5$	403.4	2.5	1.1×10^{-7}	6.7
Collis 20%	Boscalid[F]	$C_{18}H_{12}Cl_2N_2O$	343.2	3.0	7.2×10^{-4}	4.6
Altair® Plus 40%	Chlorpropham[H]	$C_{10}H_{12}ClNO_2$	213.7	3.8	24	110
Moncut 50%	Flutolanil[F]	$C_{17}H_{16}F_3NO_2$	323.3	3.2	4.1×10^{-4}	8.0
Vincit Minima 2.5%	Flutriafol[F]	$C_{16}H_{13}F_2N_3O$	301.3	2.3	4.0×10^{-4}	95
Rokenyl* 50%	Isoxaben[H]	$C_{18}H_{24}N_2O_4$	332.4	3.9	5.5×10^{-4}	0.9
Intrepid Pro 24%	Methoxyfenozide[I]	$C_{22}H_{28}N_2O_3$	368.5	3.7	1.3×10^{-2}	3.3
Systhane® Forte 24%	Myclobutanil[F]	$C_{15}H_{17}ClN_4$	288.8	2.9	0.2	132
Deurinol® 45 F 45%	Napropamide[H]	$C_{17}H_{21}NO_2$	271.4	3.3	2.2×10^{-2}	74
Sportak E 45 %	Prochloraz[F]	$C_{15}H_{16}Cl_3N_3O_2$	376.7	3.5	0.2	26
Promess Plus 60.5%	Propamocarb[F]	$C_9H_{20}N_2O_2$	188.3	0.8	730	9.0×10^5
Kerb* Flo 40%	Propyzamide[H]	$C_{12}H_{11}Cl_2NO$	256.1	3.3	5.8×10^{-2}	9.0
Luna Devotion 25%	Triadimenol[F]	$C_{14}H_{18}ClN_3O_2$	295.8	3.2	5.0×10^{-4}	72

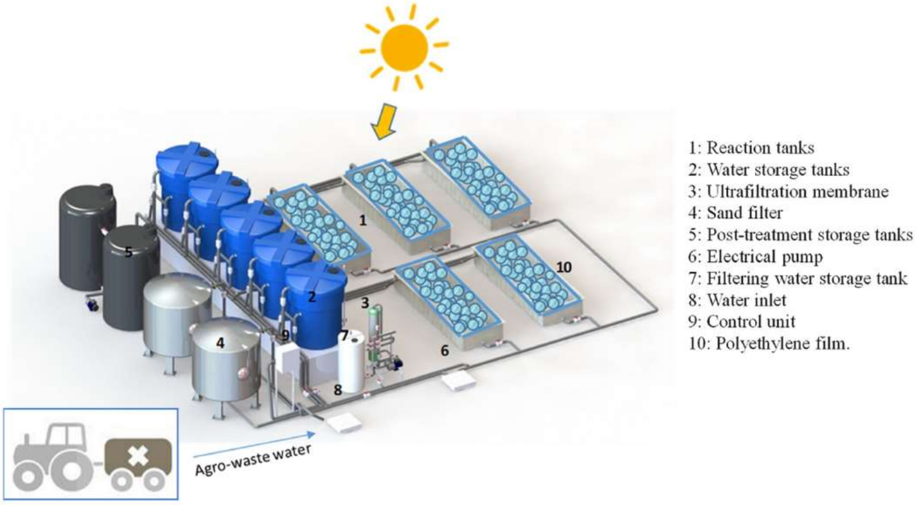

Fig. 1. Pilot plant used for decontamination of agro-wastewater under solar irradiation.

knowledge, the impact of the use of reclaimed water with these photo-processes to irrigate crop grown in field conditions is still scarce. Vela et al. (2019) used agro-wastewater treated with persulfate and sunlight for broccoli irrigation without observing reduction in the quality of the harvested product neither risks to human health.

Lettuce (*Lactuca sativa* L.) is one of the most significant horticultural crops in Spain. It represents 8.8% of horticultural cultivated surface and almost 6.2% of the total production of vegetables. Approximately, two thirds of the total lettuce production is yield in Murcia and Andalucía regions (Ministerio de Agricultura, Pesca y Alimentación, 2018). Therefore, the objective of this work was to evaluate the lettuce quality grown using treated agro-wastewater from washing of containers and phytosanitary treatments machinery. The optimal Advanced Oxidation Process (homogeneous or heterogeneous) to degrade 13 pesticide residues in agro-wastewater was investigated using a pilot facility exposed to solar radiation.

2. Materials and methods

2.1. Pesticides and reagents

Analytical standards (purity grade > 95%) and commercial formulations of the pesticides were supplied from Dr. Ehrenstorfer GmBh (Augsburg, Germany) and FitoDolores S.L. (Murcia, Spain), respectively. The main physical-chemical properties of all pesticides are summarized in Table 1 (Lewis et al., 2016).

Solvent (acetonitrile) and reagents (sodium persulfate, sodium chloride, formic acid, nitric acid 65%, perchloric acid 70% and sodium bicarbonate) were obtained from Scharlab (Barcelona, Spain). Milli-RX Water Purification System (Millipore, Bedford, MA, USA) was used to obtain pure water.

2.2. Experimental setup at laboratory scale

The amounts of photocatalyst (TiO_2, ZnO, Fe^{2+} and Fe^{3+}) and oxidants ($Na_2S_2O_8$ and H_2O_2) in different photocatalytic systems (heterogeneous and homogeneous) were previously optimized using pyrex glass vessels (110 mm length x 80 mm i. d.) containing 500 mL of irrigation water from the Tagus-Segura Water Transfer (DOC: 1.69 mg L^{-1}; EC: 0.81 dS m^{-1}; pH: 8.2; total anions: 368.77.7 mg L^{-1}; total cations 153.5 mg L^{-1}) spiked at 0.1 mg L^{-1} of each pesticide with commercial formulations, continuously stirred and exposed to sunlight for 120 min (1–3 P.M.). 989.3 ± 66.6, 14.5 ± 4.0 and 1.0 ± 0.3 (all in W m^{-2}) of VIS plus NIR, UVA and UVB radiation, respectively, were recovered at noon.

For this purpose, in $TiO_2/Na_2S_2O_8$ or $ZnO/Na_2S_2O_8$ systems, the load of the catalyst was studied ranging from 50 to 500 mg L^{-1} of TiO_2 or ZnO. Thereafter, the effect of $Na_2S_2O_8$ on the abatement of pesticides was tested using different concentrations of persulfate (from 50 to 500 mg L^{-1}). For Fenton systems, different concentrations of Fe^{2+}/Fe^{3+} (5–80 mg L^{-1}) and H_2O_2 (20–120 mg L^{-1}) were assessed to optimize the Fenton's reagent (FR) at two pH level (3 and 5).

2.3. Experimental design at pilot plant scale

Fig. 1 shows the drawing of the facility located in Torreblanca (Murcia, SE of Spain, latitude 38° 01′ 15″ N, longitude 1° 09′ 56″ W),

Table 2
Irrigation and fertilization programs followed during growing of lettuce.

Date	Irrigation time (min)	Water source		Fertilization *per* type of water used				
		Plots 1-4	Plots 5-8	H_2KPO_4 (g)	KNO_3 (g)	$Ca(NO_3)_2$ (g)	$MgSO_4$ (g)	NH_4NO_3 (g)
25/10/18		**Planting**						
25/10/18	125	TW	T-S WT	125	–	–	–	–
26/10/18	75	TW	T-S WT	75	–	–	–	–
29/10/18	109	TW	T-S WT	109	56	84	–	–
08/11/18	41	TW	T-S WT	41	–	–	33	–
12/11/18	57	TW	T-S WT	57	17	60	–	48
21/11/18	–	TW	T-S WT	–	–	–	–	–
27/11/18	40	TW	T-S WT	40	–	–	90	–
03/12/18	60	TW	T-S WT	60	20	72	–	41
07/12/18	60	TW	T-S WT	60	13	63	–	31
10/12/18	30	TW	T-S WT	30	–	–	–	–
11/12/18	45	TW	T-S WT	45	–	–	65	–
14/12/18	50	TW	T-S WT	50	17	74	–	34
17/12/18	50	TW	T-S WT	50	–	–	52	–
19/12/18	45	TW	T-S WT	45	19	89	–	37
21/12/18	45	TW	T-S WT	45	–	–	67	–
24/12/18	40	TW	T-S WT	40	–	–	–	–
26/12/18	40	TW	T-S WT	40	25	120	–	50
28/12/18	40	TW	T-S WT	40	–	–	80	–
02/01/19	40	TW	T-S WT	40	30	150	–	60
04/01/19	30	TW	T-S WT	30	–	–	80	–
08/01/19	55	TW	T-S WT	55	32	222	–	62
11/01/19	40	TW	T-S WT	40	–	–	85	–
14/01/19		**Harvesting**						

T-S WT: Tagus-Segura Water Transfer; TW: treated water.

Table 3
Analytical conditions of the studied pesticides by HPLC-MS^2.

Pesticide	t_R (min)[a]	SRM_1/SRM_2 (*m/z*)[b]	VF_1/VF_2 (V)[c]	EC_1/EC_2 (V)[d]
Propamocarb	3.0	189 → 102	90	10
	5.8	189 → 144	90	10
Flutriafol	21.7	302 → 70	110	10
		302 → 123	110	20
Prochloraz	23.9	376 → 308	90	5
		376 → 70	90	20
Triadimenol	24.0	296 → 70	70	5
	24.5	296 → 99	70	10
Azoxystrobin	25.7	404 → 372	110	10
		404 → 344	110	20
Myclobutanil	25.8	289 → 70	130	15
		289 → 125	130	40
Boscalid	25.9	343 → 307	130	20
		343 → 140	130	20
Napropamide	26.3	272 → 199	110	5
		272 → 171	110	10
Propyzamide	26.5	256 → 190	70	10
		256 → 173	70	10
Isoxaben	26.7	333 → 165	90	10
		333 → 85	90	5
Methoxyfenozide	26.8	369 → 149	90	10
		369 → 133	90	20
Chlorpropham	26.9	214 → 172	90	5
		214 → 154	90	10
Flutolanil	27.6	324 → 242	110	20
		324 → 262	110	10

[a] Retention time.
[b] Single reaction monitoring transitions (m/z).
[c] Fragmentor.
[d] Collision Energy.

previously described by Kushniarou et al. (2019) and used to carry out the solar photocatalysis experiment during the summer-autumn 2018. The pilot plant facility consists of five open reaction tanks (300 × 100 × 40 cm) connected to water storage tanks and recovery system for TiO_2 nanopowder consisting of an ultrafiltration membrane type filter enclosed in a Mann + Hummel U860 cartridge (165 cm long, 23 cm diameter). The storage tanks are enabled to accumulate water up to 1000 L. The water is transferred to the reaction tanks by natural pressure difference. Then, the catalyst and oxidant are added. Periodically, air was injected into the tank. The tanks are drained with the aid of pump and the water is passed through the ultrafiltration membrane. Finally, the clean water is accumulated in two post-treatment tanks (2000 L each) of storage.

Irrigation water was also used in this experiment to simulate washing of machinery used in phytosanitary treatment carried out in the wash zone. The total volume to treat was approximately 5000 L. For detoxification experiment, 500 L were introduced in each reaction tanks and spiked using a calculated volume of every individual formulated pesticide in order to achieve a spiking level of approximately 100 μg L^{-1} of each pesticide. In each reaction tank were added 100 g of TiO_2 and 100 g of $Na_2S_2O_8$. High-density polyethylene (HDPE) film (density: 0.95 g cm^{-3}; water absorption, 24 h < 0.05%) was used to cover the tanks. Finally, the same procedure was replicated two times. A photoradiometer (Skye Instruments LTD, Powys, UK) equipped with UVA and UVB sensors was used to measure UVA and UVB radiation during the photoperiod. A water sample was taken of each reaction tank at different UV accumulated. Radiant fluence ($H = dE/dA$, the radiant energy received by a surface per unit area) was used to calculate the degradation rates. Thus, the apparent rate constants (k_{app}) were obtained using SigmaPlot version 13.0 statistical software (Systat, Software Inc., San Jose, CA, USA) from the following equation:

$$C_H = C_0 e^{-k_{app}H} \quad (1)$$

where k_{app} ($time^{-1}$) is the apparent reaction rate constant, H the radiant fluence, C_0 the initial concentration of pollutant and C_H is the residual concentration of pollutant at radiant fluence H. The total degradation rate for the sum of the compounds was calculated as mean value (degradation rate) of all compounds.

2.4. Lettuce cultivation

Iceberg lettuce (*Lactuca sativa* L., var. *Mestiza*) cultivation was conducted during 81 days in a clay-loam textured soil (30% clay, 43% silt, 27% sand; pH 8.1, OC 0.5%; EC 4.8 dS m^{-1}; alkalinity 456 mg $CaCO_3$ kg^{-1}). Lettuce plants were planted in October 2018 in a greenhouse

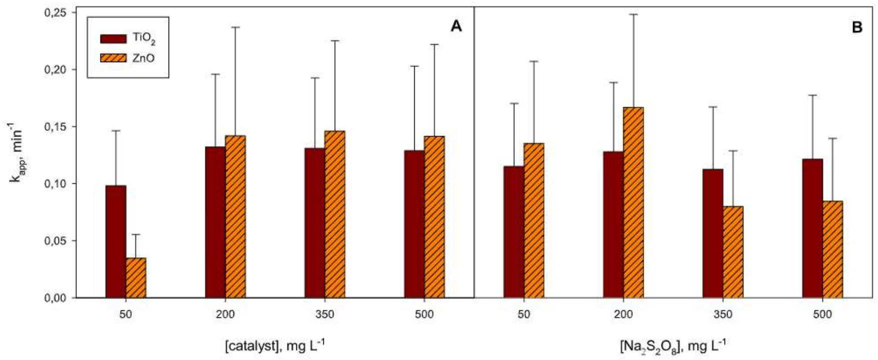

Fig. 2. Optimization of heterogeneous photocatalytic processes carried out at laboratory scale under natural sunlight. (A) Catalyst concentration (fixed $[Na_2S_2O_8] = 150$ mg L^{-1}) and (B) $Na_2S_2O_8$ concentration (fixed [photocatalyst] = 200 mg L^{-1}).

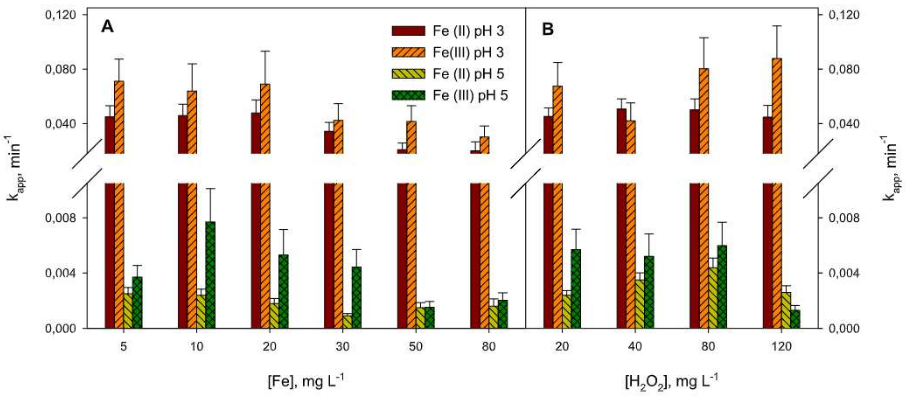

Fig. 3. Optimization of homogeneous photocatalytic processes, at pH 3 and 5, carried out at laboratory scale under natural sunlight. (A) Fe concentration (fixed $[H_2O_2] = 60$ mg L^{-1}) (B) H_2O_2 concentration (fixed [Fe] = 10 mg L^{-1}).

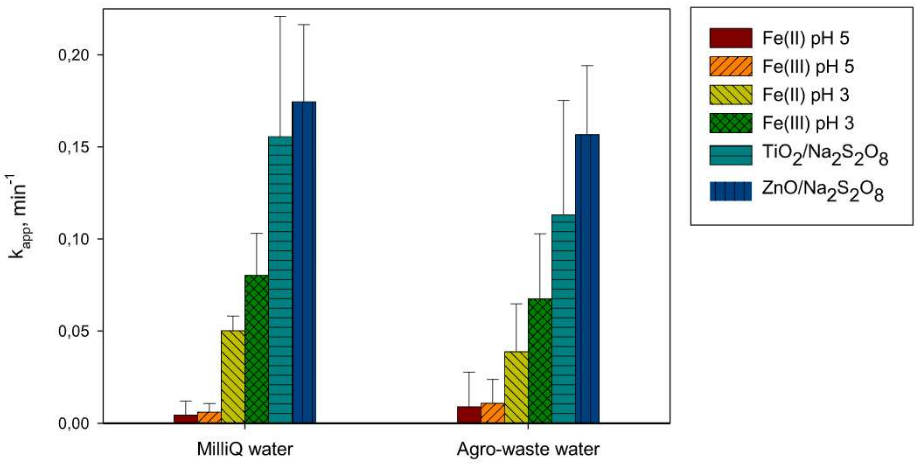

Fig. 4. Comparative study of solar photodegradation processes for studied pesticides in pure and agro-wastewater in optimal conditions.

divided into eight plots (4 × 3 m) placed in southeast Spain (Torre Pacheco, Murcia) under Mediterranean climate. The planting framework was 80 × 30 cm (78 plants per plot). Plants were irrigated by drip irrigation using 39 emitters of 1.6 L h^{-1} per plot. The water volume used was 100 L m^{-2}, approximately. Water treated and water non-treated were used for plots 1–4 and 5–8, respectively. Table 2 shows the irrigation program followed. Mineral fertilizers (KNO_3, H_2KPO_4, $Ca(NO_3)_2$, $MgSO_4$ and NH_4NO_3) were applied with each irrigation cycle according to crop needs and weather conditions. During the harvesting, soil and lettuce samples were collected of each plot. Three soil and lettuce replicates were collected for plot, each consisting of ten soil tastes and six lettuce plants, respectively. Leaching water samples were collected during cultivation.

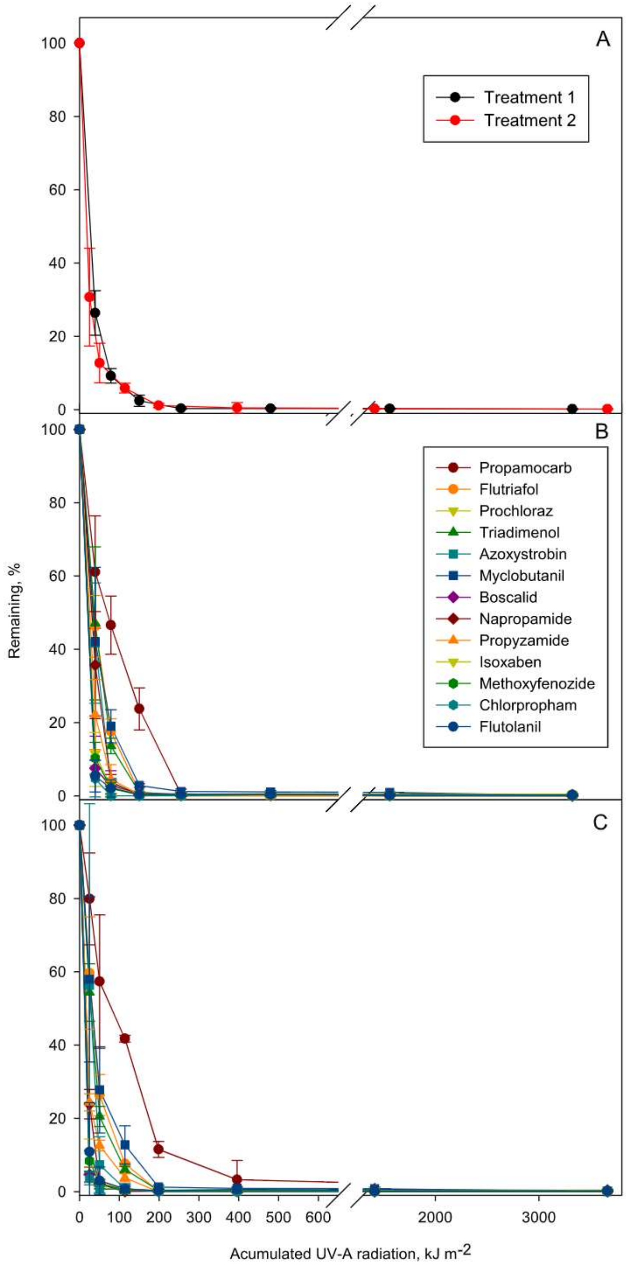

Fig. 5. Mean photocatalytic degradation of pesticides studied (A) and photocatalytic degradation of each pesticide studied during first (B) and second treatment (C) under natural sunlight at pilot plant scale using TiO_2+ $S_2O_8^{2-}$ (n = 5).

2.5. Analytical determinations

Water, soil and lettuce samples were analysed according to the procedures described by Fenoll et al. (2011, 2012a) and Vela et al. (2019), respectively. Pesticide residues were determined using an HPLC system (1200 series, Agilent Technologies, Santa Clara, USA) equipped with a triple quadrupole mass spectrometer (G6410A series, Agilent Technologies) operating in electrospray ionization (ESI) positive ion mode. Table 3 lists the analytical conditions of the pesticides. The limits of quantification (LOQ calculated S/N = 10) in water, soil and lettuce ranged from 0.04 to 1.5 μg L^{-1}, 0.07–2.6 μg kg^{-1} 0.11–3.1 μg kg^{-1}, respectively.

Dissolved organic carbon (DOC) content was measured 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).

The colour of each lettuce sample was determined by reflectance, using a Minolta CR-200 colorimeter (Ramsey, NJ, USA), in the inner and outer leaves according to the procedure defined by López et al. (2014). P_{total}, Na, K, Ca, Mg, Fe, Cu, Mn and Zn were extracted according to Chapman and Pratt (1961) and analysed by ICP-OES (Varian Vista MPX, Victoria, Australia). NO_3^-, PO_4^{3-}, Cl^- and SO_4^{2-} were extracted according to Abbas et al. (1991) and determined using a Dionex ICS-3000DC ion chromatograph (Sunnyvale, Canada) according to López et al. (2014).

2.6. 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, USA) 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 24 software (Armonk, NY, USA).

3. Results and discussion

3.1. Optimization of experiments at lab-scale under solar exposure

The optimization of photocatalytic processes was carried out in pure water at laboratory scale under natural sunlight. In heterogeneous photocatalytic processes, the effect of catalyst and $Na_2S_2O_8$ loading on the abatement of pesticides was studied. As general rule, the photocatalytic degradation of the pesticides initially increases with catalyst and $Na_2S_2O_8$ loading mainly due to the greater number of catalyst active sites available for reaction and lower possibility of e^-/h^+ recombination, respectively (Herrmann, 2010; Quiroz et al., 2011). However, high concentrations of catalyst decrease the degradation rate mainly due to screening effects (Herrmann, 2005). As result, 200 mg L^{-1} of $Na_2S_2O_8$ and 200 mg L^{-1} of catalyst were chosen as more appropriate concentrations for further experiments under natural sunlight (Fig. 2). These optimal amounts show quite good congruence with others studies (Fenoll et al., 2019; Kushniarou et al., 2019). In addition, no significant differences were observed on the rate constants when the pH was varied from 6 to 8.

In Fenton systems, the effect of catalyst and H_2O_2 concentrations on the disappearance of the studied pesticides at two pH level (3 and 5) was also investigated (Fig. 3). The optimal amount of iron (Fe^{2+} or Fe^{3+}) for carrying out photodegradation of the pesticides was 10 mg L^{-1} according to the obtained results by other authors (Gonzalez et al., 2009; Romero et al., 2016). Although, iron is not toxic to plants in aerated soils, however 10 mg L^{-1} is slightly above the threshold level of iron (5 mg L^{-1}) proposed by FAO (Pescod, 1992), WHO (2006) and US EPA (2012) for agricultural reuse of wastewater. On the other hand, H_2O_2 concentration is key parameter on the oxidation capacity of the Fenton's reagent (FR). In this case, 80 mg L^{-1} of H_2O_2 was selected as most appropriate concentrations (Fig. 3). However, a higher increase in H_2O_2 concentration can have a negative effect because it can act as $HO^\bullet$ scavenger (Mirzaei et al., 2017). Finally, the pH of the water sample had a crucial influence on the degradation of pesticides by homogeneous Fenton reaction (Zhang et al., 2019). pH 3 was determined as optimal, according to the literature (Rahim Pouran et al., 2015), although a pH adjustment is required (Fig. 3). The mono-hydroxyl complex $[Fe^{3+}(OH^-)_x (H_2O)_y]$ is the most photoactive specie, which apart from efficiently generating Fe^{2+}, produces further $HO^\bullet$. As this complex is predominant at pH ≈ 2.8, this is the reason why this pH is frequently proposed as optimal for the photo-Fenton process (Pignatello et al., 2006). Higher pH values cause a considerable decline in Fenton efficiency due to the precipitation of ferric hydroxide, which consume the catalyst, inhibit the reaction and decline the radiation transmission in photo-Fenton process. However, Goslan et al. (2006) determined a pH =

Table 4
Kinetic parameters of treatment 1 and 2.

Pesticide	Treatment 1				Treatment 2			
	R^2	k_{app} ($m^2\ kJ^{-1}$)	$S_{y/x}$	H_{50} ($kJ\ m^{-2}$)	R^2	k_{app} ($m^2\ kJ^{-1}$)	$S_{y/x}$	H_{50} ($kJ\ m^{-2}$)
Propamocarb	0.991	0.0105	3.7	66.0	0.991	0.0092	4.0	75.3
Flutriazol	0.998	0.0211	1.8	32.9	0.996	0.0237	2.5	29.2
Prochloraz	1.000	0.0647	0.8	10.7	1.000	0.1207	0.5	5.7
Triadimenol	0.995	0.0220	2.8	31.5	0.995	0.0275	2.6	25.2
Azoxystrobin	0.986	0.0268	4.6	25.9	0.970	0.0326	7.0	21.3
Myclobutanil	0.999	0.0217	0.9	31.9	0.995	0.0226	2.8	30.7
Boscalid	0.999	0.0646	0.9	10.7	0.995	0.0337	2.7	20.6
Napropamide	0.994	0.0293	3.0	23.7	0.999	0.0590	1.3	11.7
Propyzamide	1.000	0.0384	0.2	18.1	0.994	0.0511	2.8	13.6
Isoxaben	1.000	0.0545	0.6	12.7	1.000	0.0879	0.6	7.9
Methoxyfenozide	1.000	0.0573	0.5	12.1	1.000	0.0967	0.6	7.2
Chlorpropham	1.000	0.0777	0.2	8.9	1.000	0.1310	0.4	5.3
Flutolanil	1.000	0.0731	0.8	9.5	1.000	0.0863	0.8	8.0

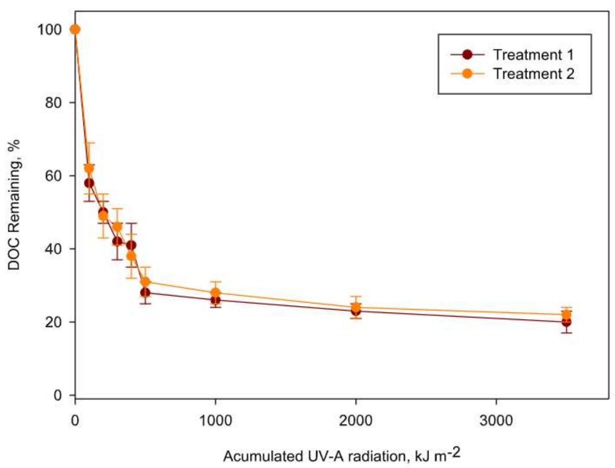

Fig. 6. Evolution of dissolved organic carbon (DOC) during the first and second photocatalytic treatments under natural sunlight at pilot plant scale using TiO_2 + $S_2O_8^{2-}$. Error bars denote standard deviation (n = 5).

4.5 as optimal, which is contradictory to the literature, although it is advantageous from an economic perspective, as no pH adjustment is required. Another reasons can be attributed to decline in oxidation potential of hydroxyl radicals and the low rate of H_2O_2 decomposition to produce $HO^{\bullet}$ due to the deficiency of H^+ ions (Mirzaei et al., 2017; Rahim Pouran et al., 2015). However, different strategies (source and dosage of iron) in the photo-Fenton process have been developed to obtain similar results at circumneutral pH, reducing operational costs (Carra et al., 2013; Clarizia et al., 2017).

3.2. Comparative study in optimal conditions of heterogeneous and homogeneous photocatalytic processes at lab-scale under solar radiation

Once the $ZnO/S_2O_8^{2-}$, $TiO_2/S_2O_8^{2-}$ and Fenton systems were optimized, a comparative study of these processes using pure and agro-wastewater was carried out under sunlight (Fig. 4). As can be observed, the efficiency in both types of water was in the order: ZnO + $S_2O_8^{2-}$ (pH 7) > TiO_2+ $S_2O_8^{2-}$ (pH 7) > Fe^{3+} (pH 3) > Fe^{2+} (pH 3) > Fe^{3+} (pH 5) > Fe^{2+} (pH 5). As general rule, the complexity of the water matrix cause an inhibitory effect in the photo-efficiency of different AOPs, because the presence of numerous co-existing species (e.g., natural organic matter, organic acids and inorganic ions) that compete with the organic pollutants for oxidant species. High chloride concentration in used agro-wastewater could be responsible of the decrease in the degradation rate in Fenton systems due to formation of complexes, such as $FeCl_2^+$ and $FeCl^{2+}$, whose reduces the ability to recycle ferrous iron (Neamţu et al., 2014).

The Fenton process initiated by Fe^{3+} is observed to be less effective than Fe^{2+} at pH 3, according to the literature (Giannakis et al., 2016). These forms of iron salts are used mostly in homogeneous Fenton oxidation systems due to negligible mass transfer limitations among these catalysts and the oxidants (Pouran et al., 2014).

The difference photoactivity of ZnO and TiO_2 may be due to the fact that ZnO can absorbs a larger fraction of solar spectrum than TiO_2. In addition, the higher electronic mobility of ZnO than TiO_2 induces lower charge recombination (Kitsiou et al., 2009). By contrast, TiO_2 presents higher specific surface area and lower particle size than ZnO. In this work, the excellent and higher activity observed for ZnO is agree with results obtained by other authors (Fenoll et al., 2012b, 2015). However,

Table 5
Quality parameters of lettuce measured (mean ± SD) after harvesting.

Parameter		Water source		Significance
		Control	Treated	
Total yield (kg)		212.5	208.3	n.s.
Weight (g)		428.5 ± 92.2	414.1 ± 118.5	n.s.
Longitudinal diameter (cm)		12.3 ± 0.9	12.4 ± 1.2	n.s.
Equatorial diameter (cm)		14.4 ± 0.9	14.2 ± 1.4	n.s.
External Colour	L*	61.9 ± 7.5	61.9 ± 5.1	n.s.
	a*	−12.9 ± 2.1	−13.6 ± 2.4	n.s.
	b*	24.5 ± 3.7	25.8 ± 4.1	n.s.
Internal Colour	L*	58.5 ± 6.8	58.8 ± 6.1	n.s.
	a*	−9.7 ± 1.9	−9.3 ± 1.5	n.s.
	b*	24.9 ± 4.1	23.8 ± 4.2	n.s.
Water (%)		92.7 ± 0.9	92.0 ± 1.1	n.s.
Mineral Composition (mmol kg^{-1})	Cl^-	1238.0 ± 109.0	1191.7 ± 109.5	n.s.
	SO_4^{2-}	106.2 ± 13.1	102.7 ± 14.7	n.s.
	NO_3^-	456.1 ± 135.1	414.9 ± 78.6	n.s.
	PO_4^{2-}	209.5 ± 29.5	196.9 ± 29.2	n.s.
	K	1183.0 ± 205.5	1127.8 ± 130.7	n.s.
	Ca	91.3 ± 15.3	83.8 ± 12.4	n.s.
	Mg	73.6 ± 11.0	67.2 ± 11.7	n.s.
	Fe	1.2 ± 0.3	1.2 ± 0.2	n.s.
	Cu	0.23 ± 0.03	0.21 ± 0.03	n.s.
	Mn	1.2 ± 0.4	1.1 ± 0.3	n.s.
	Zn	1.4 ± 0.3	1.3 ± 0.2	n.s.
	Na	228.7 ± 39.5	231.9 ± 45.9	n.s.
	P_{total}	132.3 ± 15.7	128.4 ± 17.0	n.s.

Means are not significantly different at $p > 0.05$; SD: standard deviation (n = 12).

the use of ZnO need to adjust the pH of the solution to precipitate dissolved Zn^{2+} during the photodegradation process (Fenoll et al., 2012c). According to the obtained results, the water detoxification was carried out using $TiO_2 + S_2O_8^{2-}$ due to the greater effectiveness as compared to Fenton systems and lower operating cost that ZnO.

3.3. Photocatalytic degradation of pesticides at pilot plant scale

The mean photocatalytic degradation of the pesticides (two treatments) using $TiO_2+ S_2O_8^{2-}$ is depicted in Fig. 5A. Almost complete disappearance was achieved after about 400 kJ m^{-2} of accumulated UVA radiation. Therefore, after 1 day of treatment, the remaining percentage of pesticides was <0.5% of the total initial mass. At the end of the experiment, when 3500 kJ m^{-2} were recovered the residuary percentage of pesticides was <0.15%. Fig. 5B and C shows the photocatalytic degradation of the each pesticide during first and second treatments, respectively. Similar behaviour were observed for all pesticides in both treatments.

Table 4 shows calculated kinetic parameters of pesticides using Eq (1), where the apparent rate constants and the total fluence (kJ m^{-2}) to get a 50% reduction (H_{50}) are listed. As can be observed, the kinetics of dissipation followed an apparent first-order degradation curve in all cases, with a coefficient of determination (R^2) ranging from 0.986 to 1.000 ($S_{y/x} < 4.6$) for treatment 1 and 0.970–1.000 for treatment 2 ($S_{y/x} < 7.0$).

According to the mean rate constants, the photocatalytic oxidation sequence for the pesticides studied in agro-waste waters using TiO_2/$Na_2S_2O_8$ system was as follows:

Chlorpropham > flutolanil > methoxyfenozide ≈ prochloraz > isoxaben > boscalid > propyzamide > napropamide > azoxystrobin > triadimenol > flutriazol ≈ myclobutanil > propamocarb.

The total fluence (kJ m^{-2}) to get a 50% reduction (H_{50}) ranged from 5.3 to 75.3 kJ m^{-2} for chlorpropham and propamocarb, respectively. No significant differences ($p > 0.05$) were observed when different treatments were carried out.

The initial concentrations of DOC were 8.1 and 7.8 mg L^{-1} in agro-wastewater for treatment 1 and 2, respectively. After solar treatment, the remnant was about 21% (Fig. 6). This can be mainly due to the generation of reaction intermediates and some adjuvants present in commercial formulations. Electrical conductivity and initial content of SO_4^{2-} were increased by 0.5 units and 58%, respectively, mainly due to the generation of $SO_4^{\cdot-}$ during the process.

3.4. Reuse of reclaimed water for lettuce irrigation

Over the last decade, plant uptake of pesticides due to the use of treated wastewater has received an increasing attention (Riemenschneider et al., 2016). Therefore, there is a strong need to know the quality of fruits and vegetables growing under irrigation with reclaimed wastewater.

Table 5 shows weight, longitudinal and equatorial diameters, colour parameters, water content and mineral composition of the vegetables measured after harvesting. Colour is one of the main characteristics affecting consumer choice, playing a key role in lettuce acceptability. No significant differences ($p > 0.05$) were observed when comparing the colour of the outer leaves in lettuce grown using treated and non-treated agro-wastewater. In reference to the colour intensity of the inner leaves, no differences ($p > 0.05$) were observed between treatments. As can be also perceived no significant differences ($p > 0.05$) were detected in any case for weight, longitudinal and equatorial diameters, water content and mineral composition of the vegetables (Table 5). Finally, none of the studied pesticides was found at level above the LOQ in lettuce samples, soil and leaching water after irrigation with reclaimed water. Similar results in the quality of harvested product and absence of risks to human health were obtained by Vela et al. (2019) in broccoli grown using agro-wastewater reclaimed with persulfate. In general, a wide range of organic pollutants can be uptaked, translocated and accumulated in crop tissues. However, the risks to human health is relatively low. In addition, these risks can be reduced due to degradation and transformation processes of theses pollutants in plants (Paranychianakis et al., 2014).

4. Conclusions

Large volumes of wastewater contaminated with pesticides are generated by agricultural activities. Irrigation of plants with agro-wastewater may lead to the entry of pesticides in agricultural soils and the subsequent contamination of crops. Therefore, the risk linked to the use of these agro wastewater should be reduced in order to preserve the environment and consumer health. In this context, heterogeneous and homogeneous photocatalysis allows to regenerate agro-wastewater using natural solar radiation, a renewable and abundant energy source. These processes have been compared in order to establish their efficiency, which was in the order: $ZnO + S_2O_8^{2-}$ (pH 7) > $TiO_2+ S_2O_8^{2-}$ (pH 7) > Fe^{3+} (pH 3) > Fe^{2+} (pH 3) > Fe^{3+} (pH 5) > Fe^{2+} (pH 5). The environmentally friendly process using $TiO_2+ S_2O_8^{2-}$ was selected due to the greater effectiveness and lower operating cost that ZnO. According to obtained results, a large volume of agro-wastewater polluted with 13 pesticides has been successfully regenerated. After about 1 day of treatment (400 kJ m^{-2} of accumulated UV-A) in a pilot plant, the proportion of oxidized pesticides was >99.5%. Finally, treated water was reused for lettuce irrigation without reducing its quality. Currently, there is a strong need to increase the knowledge on the evaluation the fruit and vegetables quality grown using treated wastewater. The use of this simple and cheap technology allows the reuse of agro-wastewater, reducing the risk for human health and environment.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

M. Aliste: Investigation, Writing - original draft. **I. Garrido:** Investigation. **P. Flores:** Investigation. **P. Hellín:** Investigation. **N. Vela:** Investigation. **S. Navarro:** Investigation. **J. Fenoll:** Investigation, Writing - original draft.

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References

Abbas, M.A., Younis, M.E., Shukry, W.M., 1991. Plant-growth, metabolism and adaptation in relation to stress conditions. XIV. Effect of salinity on the internal solute concentrations in *Phaseolus vulgaris*. J. Plant Physiol. 138, 722–727. https://doi.org/10.1016/S0176-1617(11)81322-2.

Ahmed, S., Rasul, M.G., Brown, R., Hashib, M.A., 2011. Influence of parameters on the heterogeneous photocatalytic degradation of pesticides and phenolic contaminants in wastewater: a short review. J. Environ. Manag. 92, 311–330. https://doi.org/10.1016/j.jenvman.2010.08.028.

Antoniou, M.G., Shoemaker, J.A., De La Cruz, A.A., Dionysiou, D.D., 2008. Unveiling new degradation intermediates/pathways from the photocatalytic degradation of microcystin-LR. Environ. Sci. Technol. 42, 8877–8883. https://doi.org/10.1021/es801637z.

Carra, I., Casas López, J.L., Santos-Juanes, L., Malato, S., Sánchez Pérez, J.A., 2013. Iron dosage as a strategy to operate the photo-Fenton process at initial neutral pH. Chem. Eng. J. 224, 67–74. https://doi.org/10.1016/j.cej.2012.09.065.

Chapman, H.D., Pratt, P.F., 1961. Methods of Analysis for Soils, Plant and Waters. University of California, Division of Agriculture Publications, Berkeley, California.

Clarizia, L., Russo, D., Somma, I.D., Marotta, R., Andreozzi, R., 2017. Homogeneous photo-Fenton processes at near neutral pH: a review. Appl. Catal., B 209, 358–371. https://doi.org/10.1016/j.apcatb.2017.03.011.

Fenoll, J., Hellín, P., Martínez, C.M., Flores, P., Navarro, S., 2011. Determination of 48 pesticides and their main metabolites in water samples by employing sonication and liquid chromatography-tandem mass spectrometry. Talanta 85, 975–982. https://doi.org/10.1016/j.talanta.2011.05.012.

Fenoll, J., Hellín, P., Martínez, C.M., Flores, P., Navarro, S., 2012a. High performance liquid chromatography-tandem mass spectrometry method for quantifying phenylurea herbicides and their main metabolites in amended and unamended soils. J. Chromatogr., A 1257, 81–88. https://doi.org/10.1016/j.chroma.2012.08.014.

Fenoll, J., Hellín, P., Martinez, C.M., Flores, P., Navarro, S., 2012b. Semiconductor-sensitized photodegradation of s-triazine and chloroacetanilide herbicides in leaching water using TiO_2 and ZnO as catalyst under natural sunlight. J. Photochem. Photobiol. Chem. 238, 81–87. https://doi.org/10.1016/j.jphotochem.2012.04.017.

Fenoll, J., Hellín, P., Martinez, C.M., Flores, P., Navarro, S., 2012c. Semiconductor oxides-sensitized photodegradation of fenamiphos in leaching water under natural sunlight. Appl. Catal., B 115–116, 31–37. https://doi.org/10.1016/j.apcatb.2011.12.023.

Fenoll, J., Garrido, I., Cava, J., Hellín, P., Flores, P., Navarro, S., 2015. Photometabolic pathways of chlorantraniliprole in aqueous slurries containing binary and ternary oxides of Zn and Ti. Chem. Eng. J. 264, 720–727. https://doi.org/10.1016/j.cej.2014.12.015.

Fenoll, J., Garrido, I., Flores, P., Hellín, P., Vela, N., Navarro, G., Navarro, S., 2019. Implementation of a new modular facility to detoxify agro-wastewater polluted with neonicotinoid insecticides in farms by solar photocatalysis. Energy 175, 722–729. https://doi.org/10.1016/j.energy.2019.03.118.

Giannakis, S., Polo Lopez, M.I., Spuhler, D., Sanchez Perez, J.A., Fernandez Ibañez, P., Pulgarin, C., 2016. Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction. Part 1: a review of the mechanisms and the fundamental aspects of the process. Appl. Catal., B 199, 199–223. https://doi.org/10.1016/j.apcatb.2016.06.009.

Gonzalez, O., Sans, C., Esplugas, S., Malato, S., 2009. Application of solar advanced oxidation processes to the degradation of the antibiotic sulfamethoxazole. Photochem. Photobiol. Sci. 8, 1032–1039. https://doi.org/10.1039/b822658j.

Goslan, E.H., Gurses, F., Banks, J., Parsons, S.A., 2006. An investigation into reservoir NOM reduction by UV photolysis and advanced oxidation processes. Chemosphere 65, 1113–1119. https://doi.org/10.1016/j.chemosphere.2006.04.041.

Herrmann, J.M., 2005. Heterogeneous photocatalysis: State of the art and present applications. Top. Catal. 34, 49–65. https://doi.org/10.1007/s11244-005-3788-2.

Herrmann, J.M., 2010. Photocatalysis fundamentals revisited to avoid several misconceptions. Appl. Catal., B 99, 461–468. https://doi.org/10.1016/j.apcatb.2010.05.012.

Kitsiou, V., Filippidis, N., Mantzavinos, D., Pouios, I., 2009. Heterogeneous and homogeneous photocatalytic degradation of the insecticide imidacloprid in aqueous solutions. Appl. Catal., B 86, 27–35. https://doi.org/10.1016/j.apcatb.2008.07.018.

Kushniarou, A., Garrido, I., Fenoll, J., Vela, N., Flores, P., Navarro, G., Hellín, P., Navarro, S., 2019. Solar photocatalytic reclamation of agro-waste water polluted with twelve pesticides for agricultural reuse. Chemosphere 214, 839–845. https://doi.org/10.1016/j.chemosphere.2018.09.180.

Lavrnic, S., Zapater-Pereyra, M., Mancini, M.L., 2017. Water scarcity and wastewater reuse standards in Southern Europe: focus on agriculture. Water Air Soil Pollut. 228, 1–12. https://doi.org/10.1007/s11270-017-3425-2.

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk Assess. 22, 1050–1064. https://doi.org/10.1080/10807039.2015.1133242. (Accessed 1 October 2019).

López, A., García-Alonso, J., Fenoll, J., Hellín, P., Flores, P., 2014. Chemical composition and antioxidant capacity of lettuce: comparative study of regular-sized (Romaine) and baby-sized (Little Gem and Mini Romaine) types. J. Food Compos. Anal. 33, 39–48. https://doi.org/10.1016/j.jfca.2013.10.001.

Malato, S., Fernández-Ibánez, P., Maldonado, M.I., Blanco, B., Gernjak, W., 2009. Decontamination and disinfection of water by solar photocatalysis: recent overview and trends. Catal. Today 147, 1–59. https://doi.org/10.1016/j.cattod.2009.06.018.

Martínez-Piernas, A.B., Plaza-Bolaños, P., García-Gómez, E., Fernández-Ibáñez, P., Agüera, A., 2018. Determination of organic microcontaminants in agricultural soils irrigated with reclaimed wastewater: target and suspect approaches. Anal. Chim. Acta 1030, 115–124. https://doi.org/10.1016/j.aca.2018.05.049.

Ministerio de Agricultura, Pesca y Alimentación, 2018. Superficies y producciones anuales de cultivos. https://www.mapa.gob.es/es/estadistica/temas/estadisticas-agrarias/agricultura/superficies-producciones-anuales-cultivos/. (Accessed 2 September 2019).

Mirzaei, A., Chen, Z., Haghighat, F., Yerushalmi, L., 2017. Removal of pharmaceuticals from water by homo/heterogeneous Fenton-type processes - a review. Chemosphere 174, 665–688. https://doi.org/10.1016/j.chemosphere.2017.02.019.

Neamţu, M., Grandjeab, D., Sienkiewicz, A., Le Faucheur, S., Slaveykova, V., Velez Colmenares, J.J., Pulgarín, C., Felippe de Alencastro, L., 2014. Degradation of eight relevant micropollutants in different water matrices by neutral photo-Fenton process under UV_{254} and simulated solar light irradiation. A comparative study. Appl. Catal., B 158–159, 30–37. https://doi.org/10.1016/j.apcatb.2014.04.001.

Paranychianakis, N.V., Salgot, M., Snyder, S.A., Angelakis, A.N., 2014. Water reuse in EU states: necessity for uniform criteria to mitigate human and environmental risks. Crit. Rev. Environ. Sci. 45, 1409–1468. https://doi.org/10.1080/10643389.2014.955629.

Pescod, M.B., 1992. Wastewater Treatment and Use in Agriculture. Food and Agriculture Organization of the United Nations, Rome, Italy. FAO irrigation and drainage paper 47. http://www.fao.org/3/T0551E/t0551e00.htm.

Pignatello, J.J., Oliveros, E., MacKay, A., 2006. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit. Rev. Environ. Sci. Technol. 36, 1–84. https://doi.org/10.1080/10643380500326564.

Pouran, S.R., Raman, A.A.A., Daud, W.M.A.W., 2014. Review on the application of modified iron oxides as heterogeneous catalysts in Fenton reactions. J. Clean. Prod. 64, 24–35. https://doi.org/10.1016/j.jclepro.2013.09.013.

Quiroz, M.A., Bandala, E.R., Martínez-Huitle, C.A., 2011. Advanced Oxidation Processes (AOPs) for removal of pesticides from aqueous media. In: Stoytcheva, M. (Ed.), Pesticides. Formulations, Effects, Fate. InTechOpen, Mexico, pp. 685–730. https://doi.org/10.5772/1004.

Rahim Pouran, S., Abdul Aziz, A.R., Wan Daud, W.M.A., 2015. Review on the main advances in photo-Fenton oxidation system for recalcitrant wastewaters. J. Ind. Eng. Chem. 21, 53–69. https://doi.org/10.1016/j.jiec.2014.05.005.

Riemenschneider, C., Al-Raggad, M., Moeder, M., Seiwert, B., Salameh, E., Reemtsma, T., 2016. Pharmaceuticals, their metabolites, and other polar pollutants in field-grown vegetables irrigated with treated municipal wastewater. J. Agric. Food Chem. 64, 5784–5792. https://doi.org/10.1021/acs.jafc.6b01696.

Romero, V., González, O., Bayarri, B., Marco, P., Giménez, J., Esplugas, S., 2016. Degradation of Metoprolol by photo-Fenton: comparison of different photoreactors performance. Chem. Eng. J. 283, 639–648. https://doi.org/10.1016/j.cej.2015.07.091.

Tanoue, R., Sato, Y., Motoyama, M., Nakagawa, S., Shinohara, R., Nomiyama, K., 2012. Plant uptake of pharmaceutical chemicals detected in recycled organic manure and reclaimed wastewater. J. Agric. Food Chem. 60, 10203–10211. https://doi.org/10.1021/jf303142t.

US EPA, 2012. Guidelines for Water Reuse. Environmental Protection Agency, Washington, DC, USA. EPA/600/R-12/618.

Vela, N., Fenoll, J., Garrido, I., Pérez-Lucas, G., Flores, P., Hellín, P., Navarro, S., 2019. Reclamation of agro-wastewater polluted with pesticide residues using sunlight activated persulfate for agricultural reuse. Sci. Total Environ. 660, 923–930. https://doi.org/10.1016/j.scitotenv.2019.01.060.

Who, 2006. Guidelines for the Safe Use of Wastewater, Excreta and Greywater. Volume 1: Policy and Regulatory Aspects. World Health Organization, Geneva, Switzerland.

Wu, X., Dodgen, L.K., Conkle, J.L., Gan, J., 2015. Plant uptake of pharmaceutical and personal care products from recycled water and biosolids: a review. Sci. Total Environ. 536, 655–666. https://doi.org/10.1016/j.scitotenv.2015.07.129.

Zhang, M.H., Dong, H., Zhao, L., Wang, D.X., Meng, D., 2019. A review on Fenton process for organic wastewater treatment based on optimization perspective. Sci. Total Environ. 670, 110–121. https://doi.org/10.1016/j.scitotenv.2019.03.180.

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